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INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN THE EASTERN UNITED STATES

E. L. Martinez, et al

Research Triangle Institute

Prepared for:

Environmental Protection Agency

May 1974

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16. ABSTRACT

Ozone concentrations were measured continuously at ground-level at McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia between June 26 and September 30, 1973. Nitrogen dioxide and nonmethane hydrocarbon concentrations were determined at all stations during this period with the exception of McHenry, Maryland. The measurement period extended through October at Kane, Pennsylvania. Hourly ozone concentrations exceeded the National Ambient Air Quality Standard for photochemical oxidants 37, 30, 20, and 15 percent of the hours for which data are available at McHenry, Kane, Coshocton, and Lewisburg, respectively. Quality assurance studies indicated that the average relative bias for the ozone concentration measurements was ±10 percent. Nitrogen dioxide concentrations were at or near background levels throughout the study. Between-station linear correlation coefficients for hourly ozone concentration comparisons varied from .468 to .678 for simultaneous data. It was concluded that the occurrence of high ozone concentrations at nonurban locations is widespread, affecting a large area in eastern United States. A C-45 aircraft equipped with a solid-phase chemiluminescent ozone meter was used to obtain ozone concentration measurements aloft. The aircraft data support the contention that the high ozone concentrations observed at the surface were generated in the lower troposphere.

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Measurements	Nonurban		

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by

Research Triangle Institute
Research Triangle Park, N. C. 27709

Contract No. 68-02-1077

EPA Project Officer: E. L. Martinez

Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards

and

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National Environmental Research Center

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, N. C. 27711

May 1974

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Publication No. EPA-450/3-74-034

FOREWORD

During the summer and early fall of 1973 the Research Triangle Institute conducted three distinct yet closely related studies under two separate contracts with the Environmental Protection Agency. Since they are so closely related, the reporting for the three studies is presented in this volume. The principal portion of this report, which is subtitled Part 1, "Field Measurements," presents the results of an ozone and ozone precursor concentration measurement program conducted from late June through October 1973 at McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia. Part 2, subtitled "Quality Assurance Program," describes the procedures employed and the results obtained in a study designed to evaluate the interrelatability of the ozone and ozone precursor concentration measurements. Part 3, subtitled "Airborne Ozone Monitoring Program," describes the use of an instrumented C-45 aircraft to obtain ozone concentration measurements aloft. Each of the parts is complete in itself; hence, the reader interested in only one of the parts will not find it necessary to read all three in order to obtain the information he seeks.

ACKNOWLEDGMENTS

Many organizations and individuals contributed to the successful performance of the studies described herein. The Board of County Commissioners of Garrett County, Maryland, authorized the location of an air monitoring station at the Garrett County Airport; its cooperation and that of the airport manager, Mr. John Kreuzwieser, are gratefully acknowledged. An air monitoring station was located at the Kane, Pennsylvania, Area High School through the courtesy of the Kane Area School Board. Mr. Verne Johnson, principal, Mr. Ed Bryant, and Mrs. Karen Burton of the High School staff were most generous in offering their assistance; it is here acknowledged. Through the cooperation of the U.S. Department of Agriculture, an air monitoring station was located at the North Appalachian Experimental Watershed at Coshocton, Ohio. Messrs. W. Russel Hamon and William Bentz were particularly helpful to the study; their contribution is greatly appreciated. The Bendix Corporation operated a cooperative air monitoring station at Lewisburg, West Virginia, during the period of study; their contribution is also acknowledged.

Special acknowledgments are due the National Environmental Research Center at Las Vegas for providing an aircraft and pilot for the airborne ozone monitoring program. The advice and support of D. Wruble, R. Evans, and V. Andrews are greatly appreciated. Thanks also to pilot J. Knight for his flying expertise and cooperative spirit.

Finally, it is a pleasure to acknowledge the assistance of Research Triangle Institute staff members. Messrs. C. E. Moore, R. W. Murdoch, and S. R. Stilley assisted in the operation of the air quality analyzers and in data reduction. Drs. W. K. Poole and T. D. Hartwell provided guidance in the statistical analysis of air quality data. Mr. B. Crissman assisted in the preparation of graphical materials.

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INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN EASTERN UNITED STATES

Part 1. Field Measurements

by

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May 1974

INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN EASTERN UNITED STATES

Part 1. Field Measurements

1.0 INTRODUCTION

During the summer of 1972, the Research Triangle Institute (RTI) conducted an intensive study of atmospheric ozone concentrations in Garrett County, Maryland and Preston County, West Virginia.[1/] This study was predicated on earlier reports of unexpectedly high oxidant[2/] and high ozone[3/] concentrations in the study area. The 1972 study confirmed the earlier reports of high ozone concentrations; approximately 11 percent of 1043 hourly measurements made at the Garrett County Maryland Airport during the summer of 1972 exceeded the National Ambient Air Quality Standard (NAAQS) for photochemical oxidants (160 $\mu g/m^3$ not to be exceeded more than once per year). Nor was the occurrence of high ozone concentrations restricted to the Garrett County Maryland Airport--similar findings were obtained at satellite locations approximately 19 km distant. The mean hourly ozone concentration at the airport from August 4 to September 25, 1972 was 112 $\mu g/m^3$, the daytime hourly mean was 116 $\mu g/m^3$, and the nighttime hourly mean was 108 $\mu g/m^3$. The maximum hourly ozone concentration observed at the airport during the study period was 233 $\mu g/m^3$. In an urban area these concentrations would not be considered unusual and could be readily attributed to local photochemical synthesis from nitrogen dioxide and hydrocarbon precursors. In Garrett County, however, nitrogen dioxide and nonmethane hydrocarbon concentrations were at, or near, geochemical levels throughout the study period. Also, neither natural nor manmade sources in the study area appeared capable of producing the precursor quantities required for synthesis of high ozone concentrations. Ozone synthesis from naturally occurring precursors has been demonstrated;[4/] however, it was considered unlikely that this process could account for sustained

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concentrations exceeding the standard. The persistence of high ozone concentrations at night reflected the low precursor (and destructive agent) concentrations and obviously was not the result of ongoing photochemical processes. Thus, an evaluation of air quality measurements suggested that local photochemical synthesis could not account for the observed high concentrations of ozone.

Analysis of synoptic meteorological data, as well as an examination of ozone wind roses for the Garrett County Maryland Airport, indicated that the high ozone concentrations at this location developed within particular air masses which acquired their characteristics over broad regions of urban-industrial activity. High concentrations of ozone did not appear to be associated with direct transport from one or more identifiable local point or area sources of precursors. It appeared that air, moving over urban and/or industrial areas on its way to the study area, acquired ozone precursors which, upon irradiation with sunlight, yielded ozone. The sharp decrease in ozone concentration in the relatively rapidly moving air arriving behind frontal systems supported this suggestion.

The occurrence of high ozone concentrations at nonurban locations may signal a general deterioration of air quality. Indeed, Mineral King Valley and other rural California locations have experienced high oxidant concentrations.[5/] The extent to which this occurs in eastern United States, however, is unknown. The research described in this report constitutes Phase I of an investigation of the areal extent of the occurrence of high ozone concentrations at nonurban locations in eastern United States. The objectives of the research were:

1) To provide a data base of nonurban ozone and ozone precursor concentration measurements for future detailed analysis.
2) To provide statistical summaries of the frequency of occurrence of concentrations of ozone, nitrogen dioxide, and nonmethane hydrocarbons at the selected locations.
3) To determine the interrelationship between ozone concentration and concentrations of nitrogen dioxide and nonmethane hydrocarbons at the selected locations.

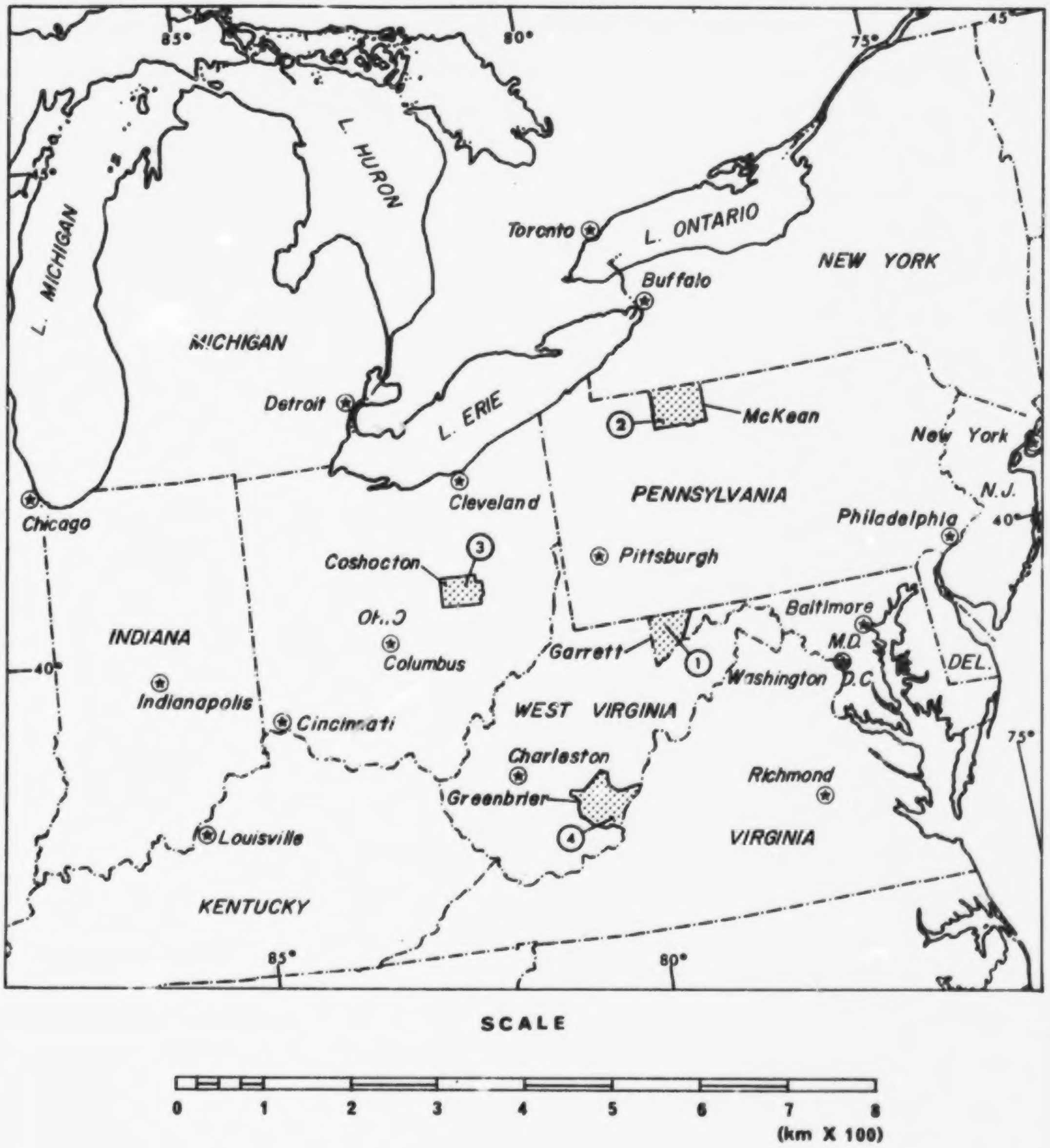
Phase II of the study will investigate the influence of synoptic-scale meteorological conditions on the ozone and ozone precursor concentrations measured at the selected locations.

2.0 PLAN OF STUDY

A summer program of concurrent field measurements of ozone and ozone precursor concentrations at nonurban locations was conducted from June through September 1973. The field measurement program employed a four-station monitoring network with stations at/or near McHenry, Garrett County, Maryland; Kane, McKean County, Pennsylvania; Coshocton, Coshocton County, Ohio; and Lewisburg, Greenbrier County, West Virginia, (Figure 1). The station at Lewisburg, West Virginia, was a cooperative station operated by the Bendix Corporation under RTI supervision. Ozone concentrations were measured at all stations, and nitrogen dioxide and nonmethane hydrocarbon concentrations were measured at all stations except McHenry, Maryland. During the study the sponsor requested that the program be supplemented by continuing measurements through October 31 at the Kane, Pennsylvania, station.

In the analysis of the data collected during the summer of 1972[1/] it was found that local surface wind speed and temperature values showed no significant relationship to the ozone concentration values. However, analysis of meteorological data on a synoptic scale suggested relationships that warranted further investigation. Accordingly, synoptic scale meteorological data collected routinely by the National Weather Service were to serve as the primary base for the Phase II analysis. Wind speed and direction were recorded at the McHenry, Maryland, and Lewisburg, West Virginia, stations for subsequent analysis as appropriate.

Ozone concentration data were collected at the four stations to provide further insight into the areal extent of the occurrence of high ozone concentrations. The frequency of occurrence of ozone, nitrogen dioxide, and nonmethane hydrocarbon concentrations was determined from an examination of the frequency distribution of hourly mean concentrations of each pollutant at each station. The statistical relationship between ozone concentrations and nitrogen dioxide concentrations was determined using correlation techniques. Lag correlation coefficients were computed to examine the association between ozone concentrations at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McKean
2
New York
N.J.
Cleveland
PENNSYLVANIA
Chicago
Philadelphia
40°
3
Coshocton
Pittsburgh
Baltimore
INDIANA
OHIO
Columbus
Garrett
1
MD.
D.C.
DEL.
Washington
40°
Indianapolis
Cincinnati
WEST VIRGINIA
75°
Charleston
Richmond
Greenbrier
4
Louisville
VIRGINIA
KENTUCKY
85°
80°
SCALE
0
1
2
3
4
5
6
7
8
(km X 100)

Station No.	*Town*	*County*
1	*McHenry*	*Garrett*
2	*Kane*	*McKean*
3	*Coshocton*	*Coshocton*
4	*Lewisburg*	*Greenbrier*

Figure 1. Ozone and ozone precursor monitoring stations (Stippled areas indicate the identified counties).

pairs of stations. Data were compared with data obtained in 1972 at McHenry, Maryland, and with the appropriate NAAQS. Data for Kane, Pennsylvania, were examined to determine what influence, if any, the change of season has on ozone concentrations.

3.0 STUDY AREAS

A discussion of the rationale for the selection of study areas and descriptions of the areas selected are presented in this section.

3.1 Selection Rationale

The rationale for selecting study areas is based on previous observations of high ozone concentrations at McHenry, Maryland. The horizontal extent of the region included in the study area was determined by considering several factors. First, station distances from McHenry must be such that there would be small risk of the stations falling outside of the suspected region of high ozone concentrations. Second, the separation between stations must be great enough to offer a reasonable expectation of having a well-defined air mass front lying between one or more pairs of stations.

Consideration of these factors led to the selection of outlying stations within approximately 250 km of the McHenry station. An additional criterion, inherent in the nature of the study, was that all stations be remote from metropolitan centers to avoid direct contamination by ozone precursors from urban-industrial activity.

McHenry, Maryland (Garrett County Airport) was the pivotal station of the sampling array. The ozone and ozone precursor data base established there in 1972 provided historical guidance and a benchmark. Without this station, there would be no way of knowing if additional measurements were characteristic or anomalous.

Kane, Pennsylvania is remote from any major population center or industrial area. The nearest principal city is Erie, Pennsylvania, 121 km to the west-northwest; Buffalo, New York is 129 km north; and Pittsburgh, Pennsylvania and Youngstown, Ohio are about 160 km to the southwest. The nearest known source of ozone precursor material is an oil refinery at Bradford, Pennsylvania, 32 km to the north; however, the general area often lies downwind of the industrial areas of Lake Michigan and Lake Erie.

Coshocton, a small town in rural east-central Ohio, is located closer to urban-industrial areas than any of the other sites selected. Akron, Canton, Youngstown, Wheeling, Columbus, and Cleveland are within a 130-km radius of Coshocton. There are several potential sources of nitrogen oxides and hydrocarbons from nearby industry.[6]

Lewisburg, West Virginia, lies in the Greenbrier River valley in the southern portion of the state. Ozone concentrations in excess of the NAAQS had been reported for this area.[7] The Lewisburg station gave a southern extension to the sampling array and provided an opportunity to measure ozone concentrations in mountainous terrain at a site other than McHenry, Maryland.

3.2 Description

Brief descriptions of the four counties in which air monitoring stations were located are given below.

3.2.1 Garrett County, Maryland

The westernmost county in Maryland, Garrett County is bounded on the east by the North Branch of the Potomac River, on the west by West Virginia, and on the north by Pennsylvania. It lies in a physiographic transition zone with both the folded Appalachian and Appalachian plateau land forms present (Figure 2). Elevation above mean sea level (MSL) varies from approximately 760 to 914m. Backbone Mountain, the highest point in Maryland, rises to 1024m MSL.

At a station located at Deep Creek the January average temperature for an 11-year period was 271.7K, while the July average was 293.1K. The maximum temperature observed at this station was 308.7K, the minimum 242.6K. The first killing frost in the fall usually occurs about October 2, ending a 130-day growing season. Annual average precipitation is about 1.14×10^3 mm.

The 1970 population of Garrett County was 21,476 and the population density was 12.6 per million m^2.

Estimated annual emissions of nitrogen oxides and hydrocarbons are 4.34×10^5 and 6.95×10^5 kg, respectively. Annual carbon

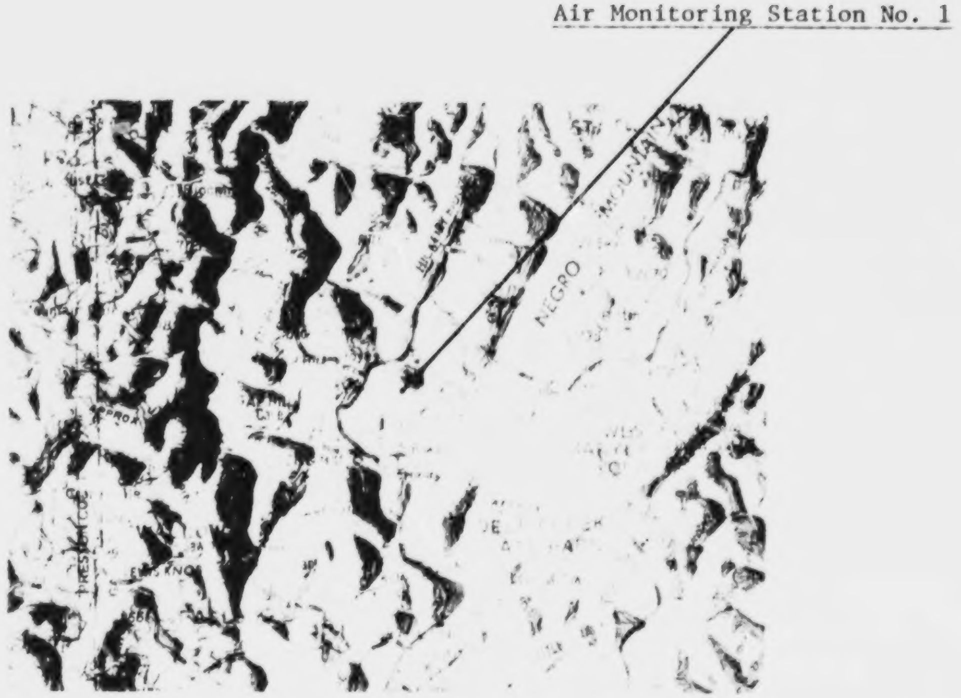
Air Monitoring Station No. 1
NEGRO MOUNTAIN

Figure 2. Photograph of a raised relief map illustrating the topography in the vicinity of the McHenry, Maryland (Garrett County Airport) monitoring station.

monoxide, particulate and sulfur dioxide emissions are estimated at 32.7×10^5, 1.48×10^5, and 3.14×10^5 kg, respectively.*

3.2.2 McKean County, Pennsylvania

Bordering New York state NNW of Pittsburgh, McKean County is typical of the Allegheny Plateau of western Pennsylvania (Figure 3). Throughout much of the county, elevations are about 610m MSL.

At Bradford the average January temperature for 14 years of record was 268.8K; the July average was 293.6K. The maximum temperature observed during the same period was 310.9K; the minimum, 242K. Growing seasons approximate 120 days, ending with the first killing frost about September 23. Annual precipitation averages about 1.07×10^3 mm.

The 1970 population of McKean County was 51,915; the population density was 20.2 per million m^2. In 1970 the Borough of Kane had a population of 5,001.

Estimated annual emissions of nitrogen oxides and hydrocarbons are 47.3×10^5 and 49.5×10^5 kg, respectively. Annual carbon monoxide, particulate, and sulfur dioxide emissions are estimated at 220.1×10^5, 85.5×10^5, and 54.8×10^5 kg, respectively.*

3.2.3 Coshocton County, Ohio

East-northeast of Columbus and SSW of Canton, Coshocton County is situated near the western terminus of the unglaciated Allegheny Plateau. The elevation of the county varies from about 229 to 335m MSL.

At the town of Coshocton, January temperatures average 271.6K and those for July average 296.9K. The maximum temperature at this station for a 23-year period was 314.2K, the minimum, 240.9K. The growing season is approximately 162 days, ending with the first killing frost in the fall about October 12. Average annual precipitation is about 1.04×10^3 mm.

The 1970 population of Coshocton County was 33,486, while the town of Coshocton had a population of 13,747. Population density for the county was 23 per million m^2.

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*Emission estimates in tons per year were provided by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency; those estimates were converted to kilograms per year.

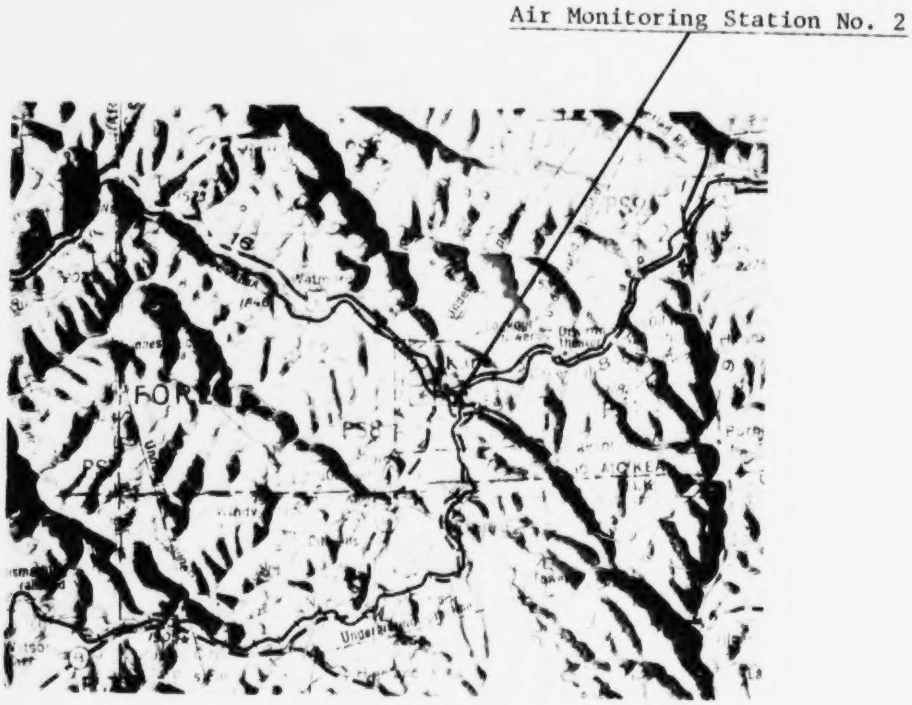
Air Monitoring Station No. 2

Figure 3. Photograph of a raised relief map illustrating the topography in the vicinity of the Kane, Pennsylvania (Kane Area Senior High School) monitoring station.

Estimated annual emissions of nitrogen oxides and hydrocarbons are 269.9 × 10^5 and 33 × 10^5 kg, respectively. Annual carbon monoxide, particulate, and sulfur dioxide emissions are estimated at 208.7 × 10^5, 223.2 × 10^5, and 1065.9 × 10^5 kg, respectively.*

3.2.4 Greenbrier County, West Virginia

East-southeast of Charleston, West Virginia, Greenbrier County is situated in the folded, or new Appalachians (Figure 4). Elevations in the county range from about 518m MSL to 1333m MSL at Grassy Knob.

At Lewisburg the average January temperature was 273.3K based on 37 years of record and the July average for the same period was 294.8K. The maximum temperature observed at this station was 312K, the minimum, 234.8K. The growing seasons is approximately 150 days, ending with killing frost about October 5. Annual precipitation averages about 1.02 × 10^3 mm.

In 1970 the population of Greenbrier County was 32,090, while the population of Lewisburg was 2,407. County population density was 12.1 per million m^2 in 1970.

Estimated annual emissions of nitrogen oxides and hydrocarbons are 13.4 × 10^5 and 19.3 × 10^5 kg, respectively. Annual carbon monoxide, particulate, and sulfur dioxide emissions are estimated at 75.6 × 10^5, 3.4 × 10^5, and 9.3 × 10^5 kg, respectively.*

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*Emission estimates in tons per year were provided by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency; those estimates were converted to kilograms per year.

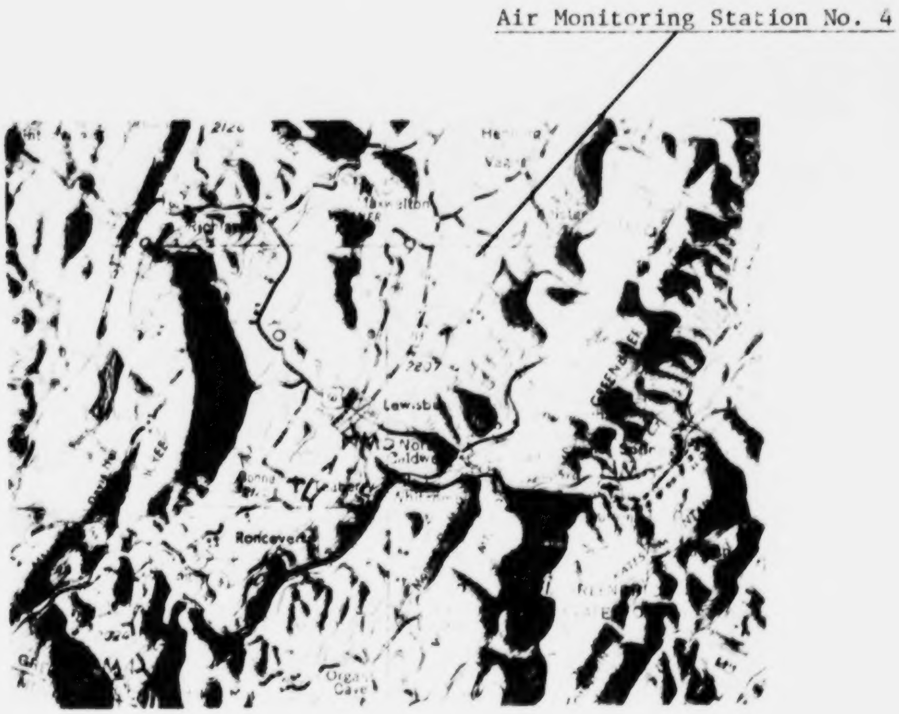

Air Monitoring Station No. 4
Ronceverte

Figure 4. Photograph of a raised relief map illustrating the topography in the vicinity of the Lewisburg, West Virginia (Greenbrier Valley Airport) monitoring station.

4.0 PROCEDURE

This section describes the procedures employed to obtain measurements of air quality and meteorological parameters. The principal criteria for the selection of a monitoring station location were:

1) that the location be free of natural and manmade obstructions to air movement;
2) that it be at a higher elevation than the surrounding terrain, and
3) that it be removed from local sources of ozone and ozone precursors.

4.1 Description of Monitoring Stations

4.1.1 McHenry, Maryland (Garrett County Airport)

The McHenry, Maryland station was located at the Garrett County Airport, approximately 884m MSL. The airport complex consists of a 762-m paved landing strip, an apron, hangars, and a terminal building. The airport is used mainly by small, private aircraft.

Figure 5 is a diagram of the airport which shows the location of the air monitoring station and the meteorological tower. While the site provided excellent exposure for the air monitoring instruments, exposure of the meteorological instruments was less than optimal. An exterior view of the station is shown in Figure 6. The aircraft shown in Figure 6 was used to transport equipment and personnel from station to station.

The only pollutant concentration measured at this station was ozone. The ozone monitor, stripchart recorder, and data acquisition system was located in a small (2.4m × 3m × 3m) workroom at the east end of the hangar. An interior view of the station is shown in Figure 7. An air conditioner was mounted in the wall to maintain temperatures near 298K. Ambient air was sampled through Teflon lines from an intake mounted 1.5m above the hangar roof. The hangar roof is about 3.7m above grade.

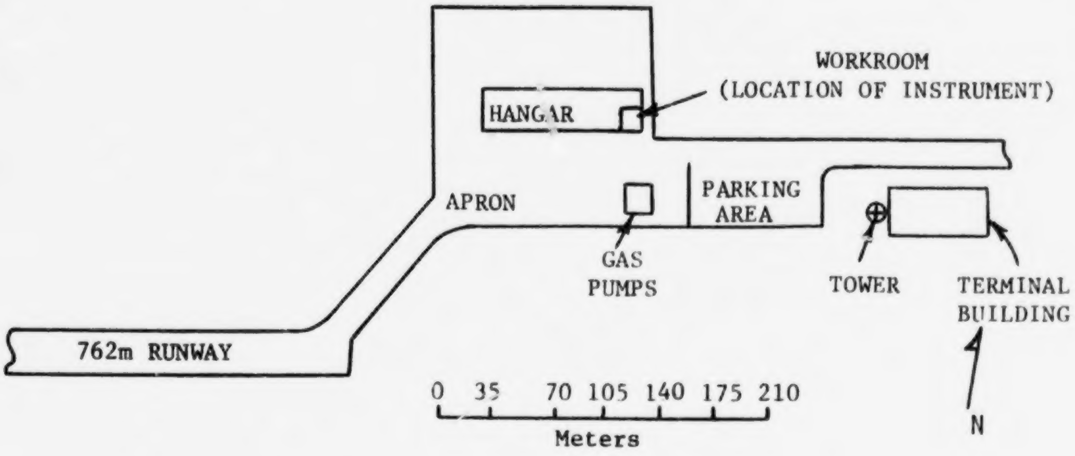

WORKROOM
(LOCATION OF INSTRUMENT)
HANGAR
APRON
PARKING AREA
GAS PUMPS
TOWER
TERMINAL BUILDING
762m RUNWAY
0 35 70 105 140 175 210
Meters
N

Figure 5. Diagram of Garrett County Airport.

Wind speed and wind direction sensors were mounted on a 9.2m tower which was braced to the terminal building. A dual channel recorder for wind speed and direction was located in the airport manager's office.

4.1.2 Kane, Pennsylvania

Surrounded on three sides by the Allegheny National Forest, the Borough of Kane is located approximately 160km north of Garrett County, Maryland. The Kane, Pennsylvania monitoring station was located in the industrial arts room of the Kane Area Senior High School. An interior view of the station is pictured in Figure 8. Situated at the highest point in the Borough (630m MSL), the school provides excellent instrument exposure from all directions. A diagram of the school grounds is shown in Figure 9.

Ozone, nitrogen dioxide, and nonmethane hydrocarbon concentrations were measured and recorded at this station. Instruments were placed on tables inside the industrial arts room. The air inlet was at a point 1.8m above the roofline. Teflon tubing connected the inlet to a glass manifold. The manifold was brought into the room through a plywood panel which replaced a window.

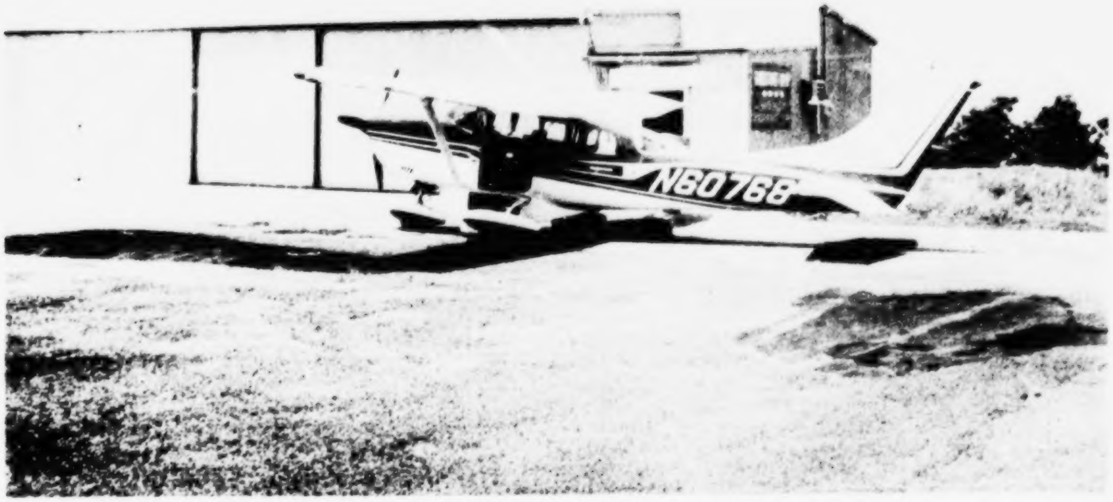


Figure 6. Exterior view of McHenry, Maryland (Garrett County Airport) station.

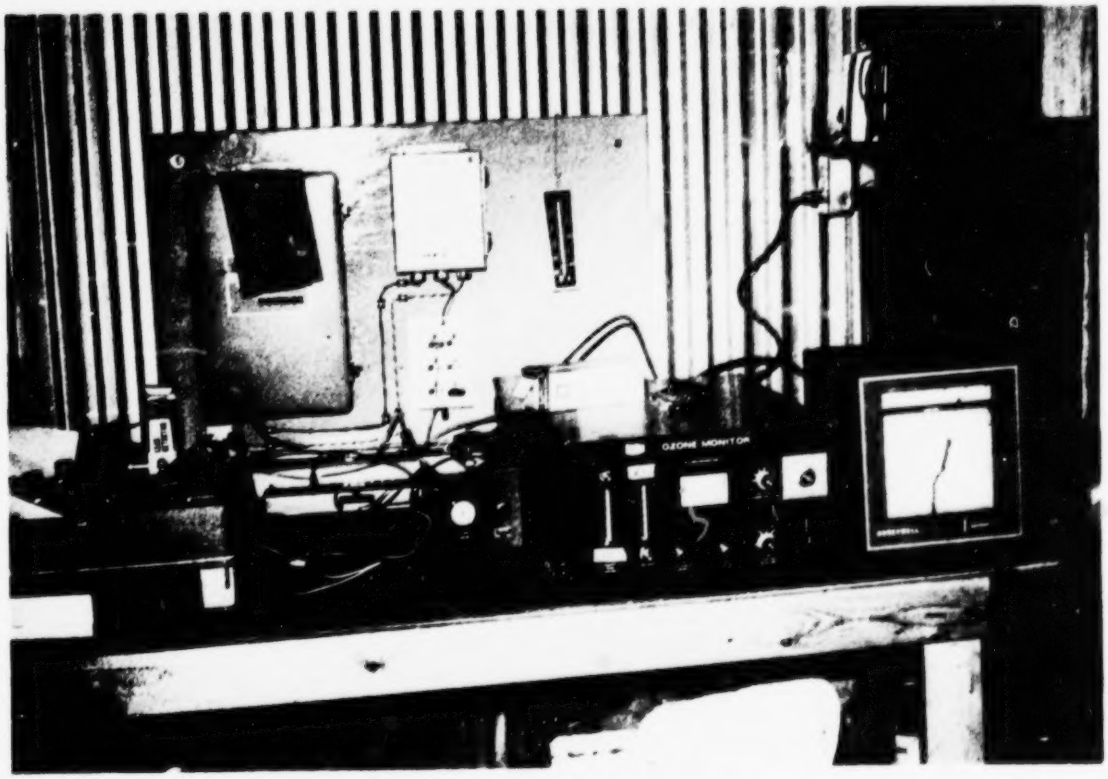

OZONE MONITOR

Figure 7. Interior view of McHenry, Maryland (Garrett County Airport) station.

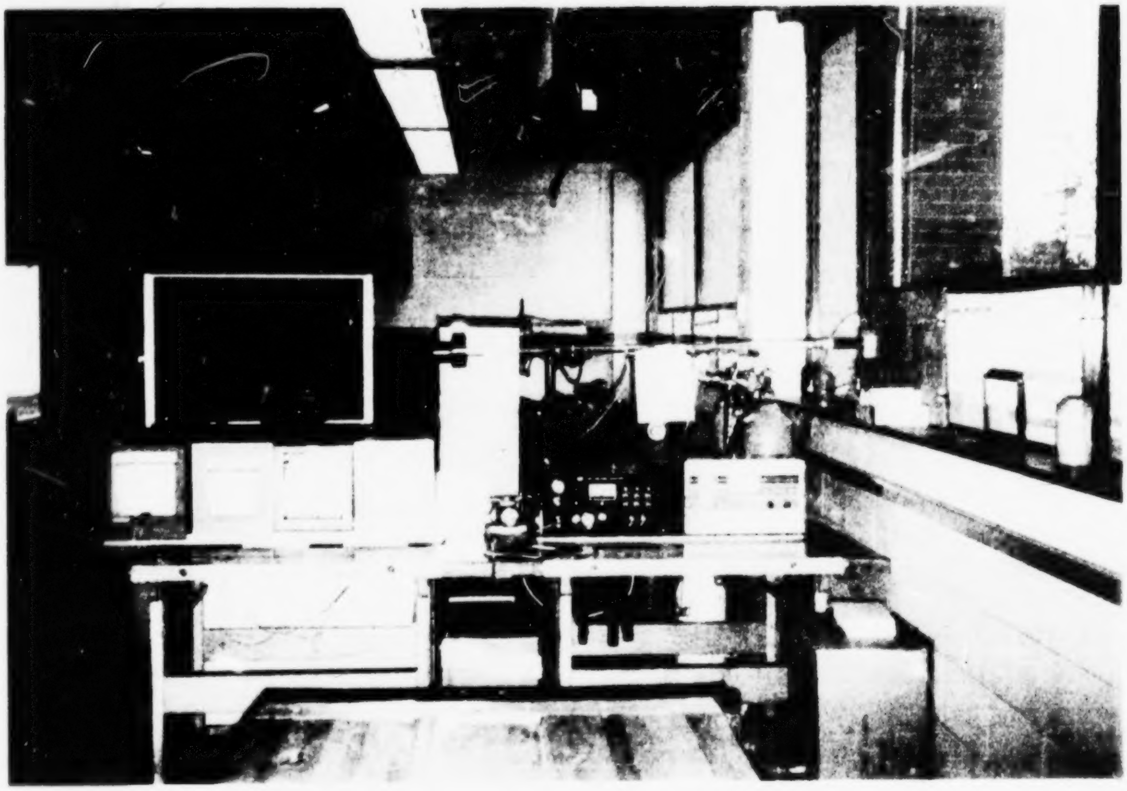
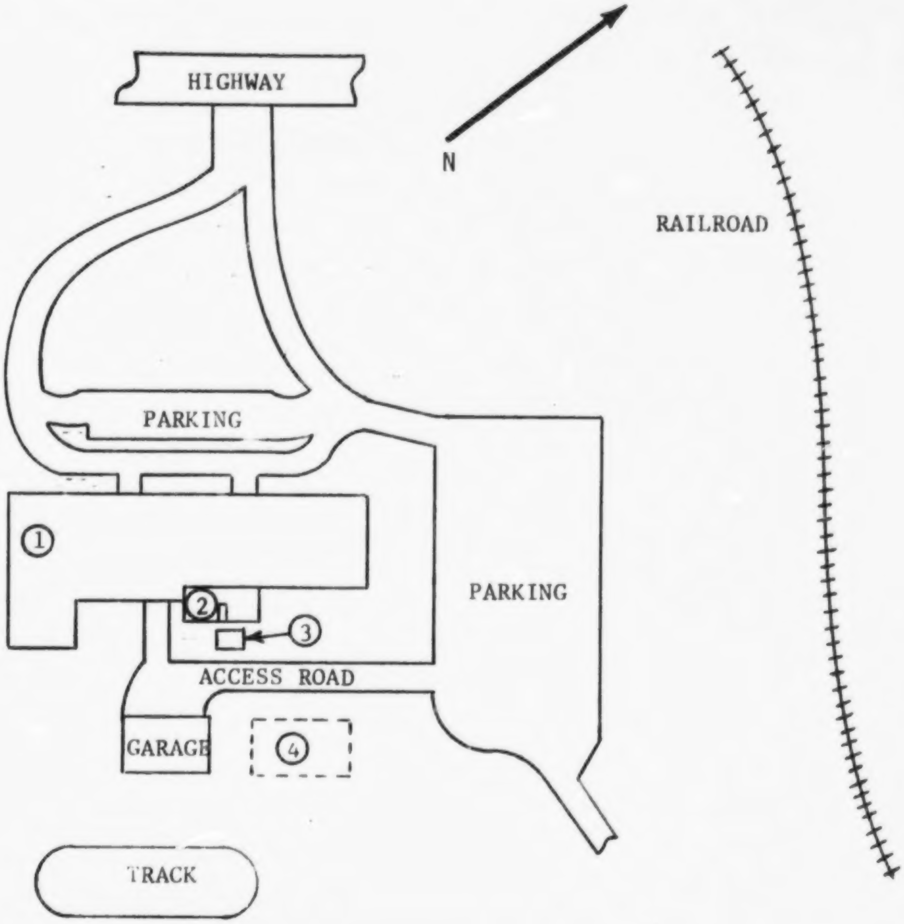


Figure 8. Interior view of Kane, Pennsylvania station.


HIGHWAY
N
RAILROAD
PARKING
①
②
③
PARKING
ACCESS ROAD
GARAGE
④
TRACK

KEY:

① High School
② Industrial Arts Room and Bench With Analyzers
③ Mobile Laboratory
④ Additional Building Constructed During Study

Figure 9. Diagram of Kane Area Senior High School and grounds.

On September 8, 1973, when classes resumed, the instruments were transferred to a mobile laboratory located immediately outside the industrial arts room. The ambient air intake was not moved. Equipment was arranged in the mobile laboratory as shown in Figure 10. The mobile laboratory is pictured in Figure 11.

4.1.3 Coshocton, Ohio

The North Appalachian Experimental Watershed 16km northeast of Coshocton was the location of the Coshocton, Ohio station. Operated by the United States Department of Agriculture, this complex of buildings is 354m MSL. The acreage surrounding the station is used mainly for farming. There are no apparent obstructions to air movement.

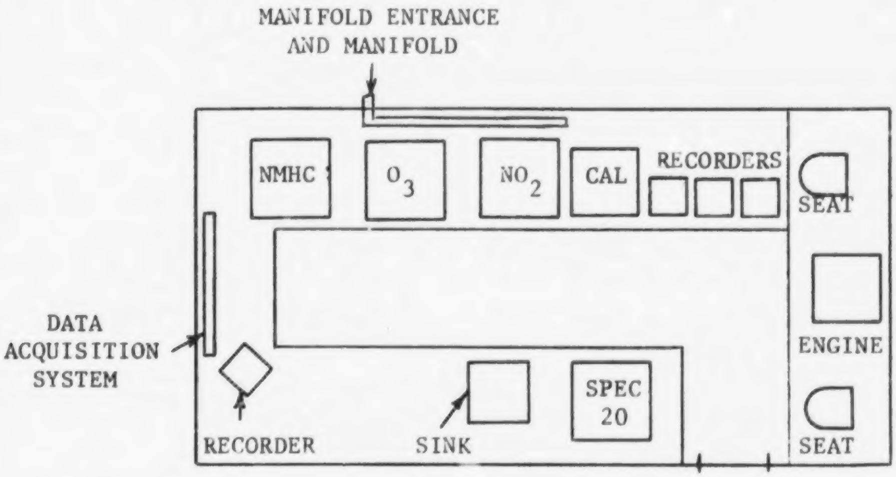

MANIFOLD ENTRANCE
AND MANIFOLD
NMHC
O_3
NO_2
CAL
RECORDERS
SEAT
DATA
ACQUISITION
SYSTEM
ENGINE
SPEC
20
RECORDER
SINK
SEAT

Figure 10. Arrangement of equipment in the mobile laboratory at the Kane, Pennsylvania station.

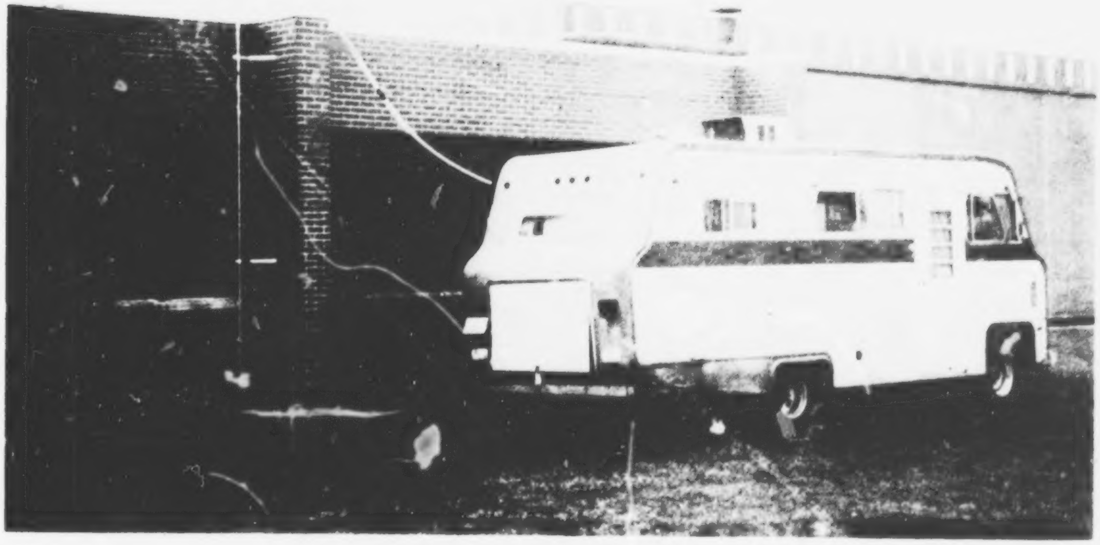


Figure 11. Mobile laboratory at the Kane, Pennsylvania station.

Nitrogen dioxide, ozone, and nonmethane hydrocarbon analyzers were housed in a room on the second floor of the Engineering Building. The room was modified by adding temporary panelling (to make a smaller room), an air conditioner, and another electrical circuit. A plan view of the station interior is shown in Figure 12 and a photograph of the equipment arrangement is shown in Figure 13.

An exterior view of the station, which shows the air intake and Teflon intake tubing is shown in Figure 14.

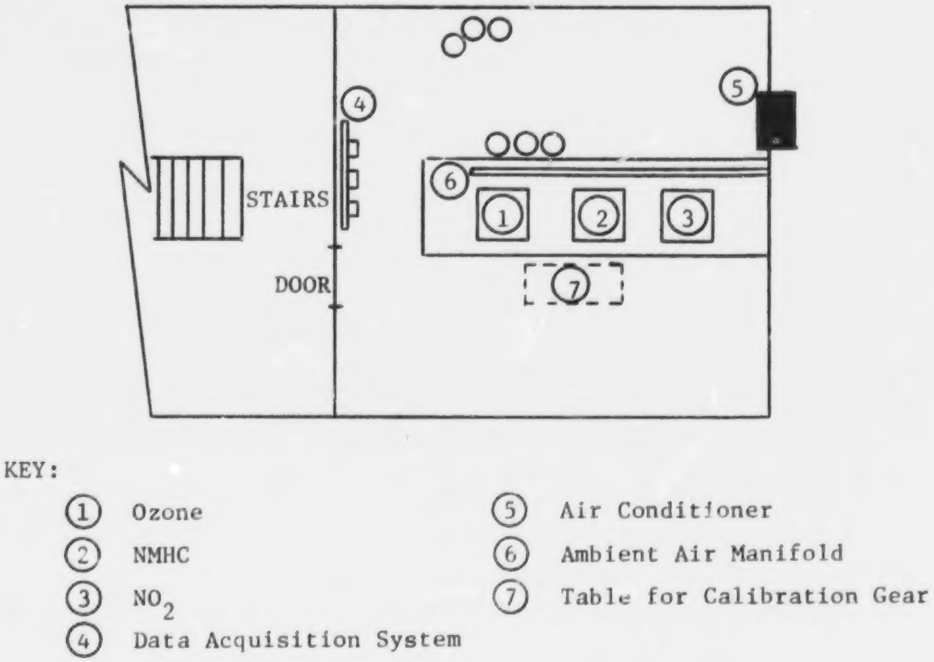

④
⑤
⑥
①
②
③
⑦
STAIRS
DOOR
KEY:
① Ozone
② NMHC
③ NO_2
④ Data Acquisition System
⑤ Air Conditioner
⑥ Ambient Air Manifold
⑦ Table for Calibration Gear

Figure 12. Plan view of interior of Coshocton, Ohio station.

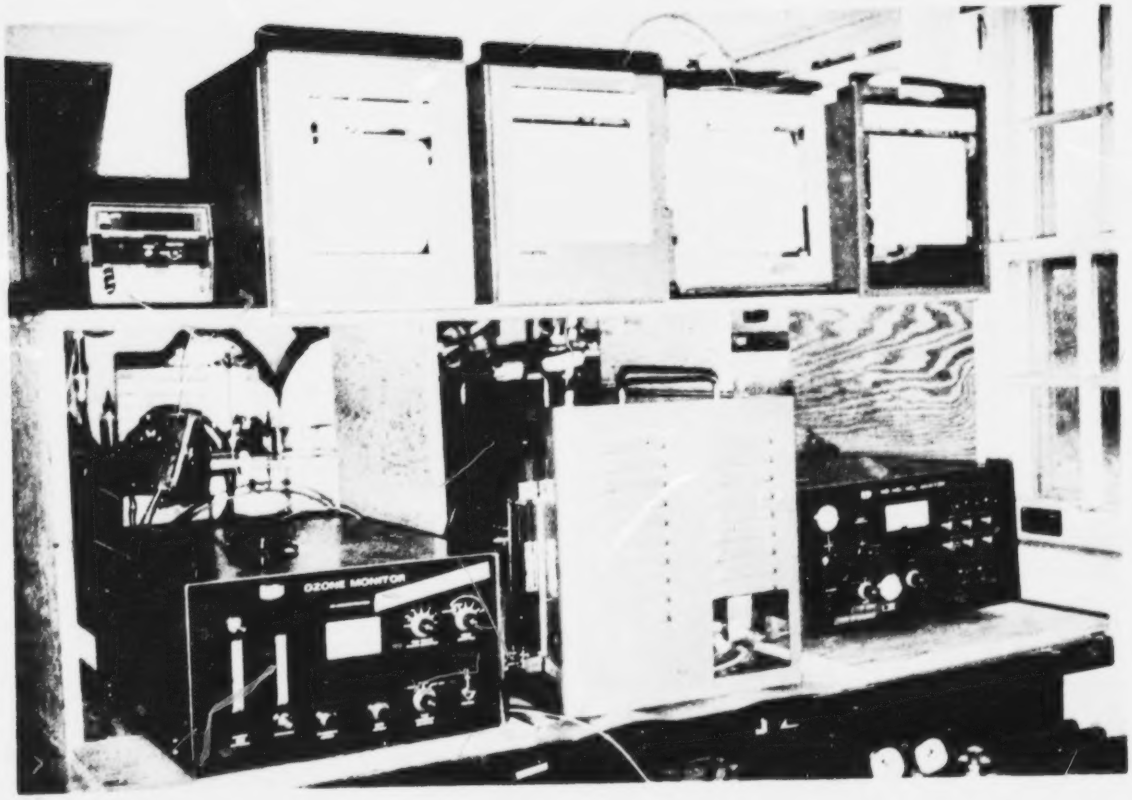

OZONE MONITOR

Figure 13. Interior view of Coshocton, Ohio station.

Figure 14. Exterior view of Coshocton, Ohio station.

4.1.4 Lewisburg, West Virginia

The Lewisburg, West Virginia station was located at the Greenbrier Valley Airport, approximately 160km southwest of Garrett County, Maryland. The airport elevation is approximately 705m MSL. The airport serves both private and commercial aviation. The valley surrounding the airport is mainly gently rolling pastureland with some wooded areas.

Analyzers and associated equipment were housed in an air-conditioned 2.5 × 9.2m mobile laboratory owned by the Bendix Corporation, Ronceverte, West Virginia. A 9.2-m, guyed tower was located 15m from the laboratory. Wind speed and wind direction transducers were mounted on it.

The general features of the airport are shown in Figure 15.

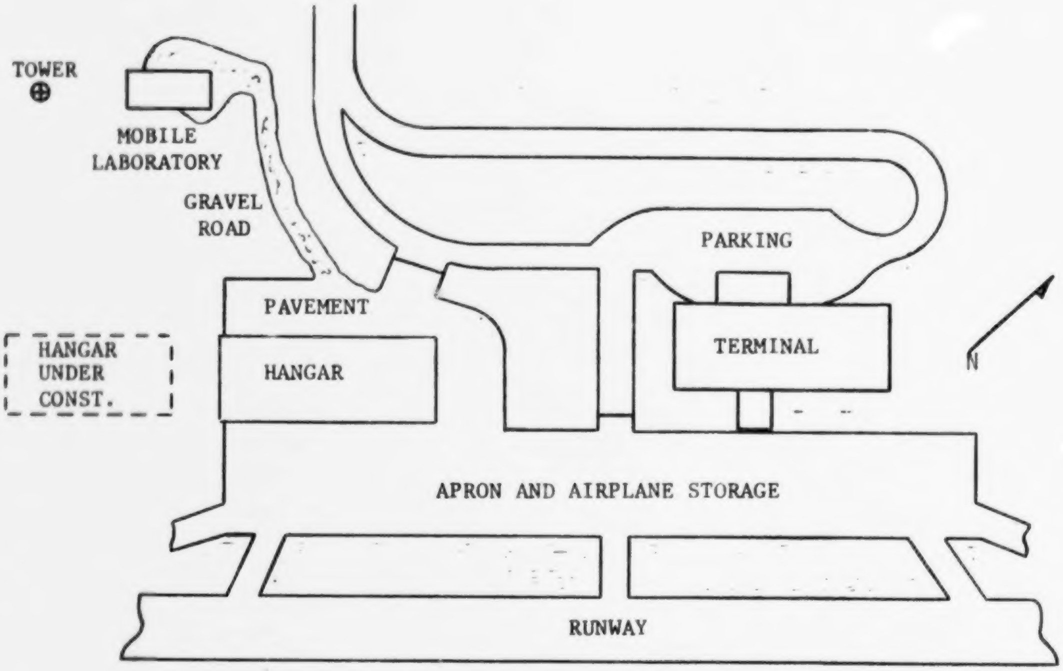
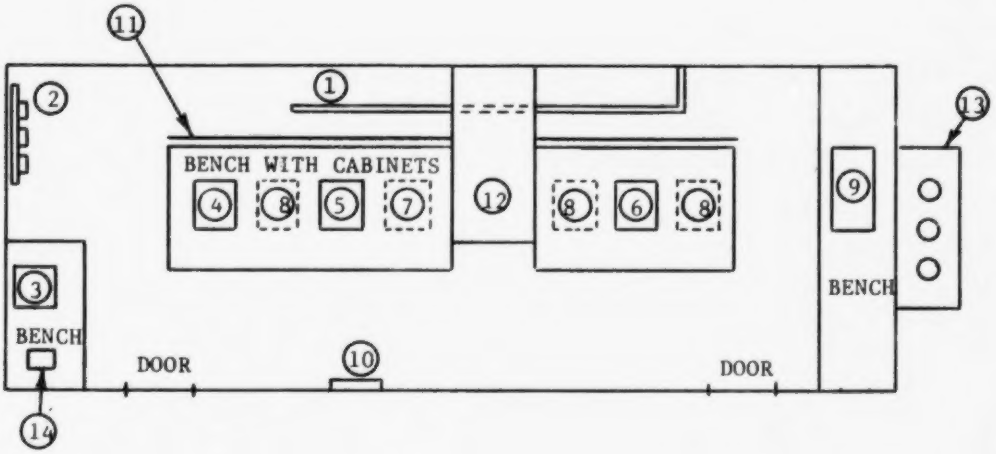

TOWER
MOBILE LABORATORY
GRAVEL ROAD
PARKING
PAVEMENT
HANGAR UNDER CONST.
HANGAR
TERMINAL
N
APRON AND AIRPLANE STORAGE
RUNWAY

Figure 15. Greenbrier Valley Airport, Lewisburg, West Virginia.

Figure 16, a diagram of the interior of the mobile laboratory, shows the location of air monitors, recorders, and the data acquisition system. An exterior view is given in Figure 17.

Ozone, nitrogen dioxide, and nonmethane hydrocarbon concentrations were measured and recorded at this station. Wind speed and wind direction were recorded intermittently.



KEY:

① Intake Manifold (mounted on ceiling enters through ceiling)

② Data Acquisition Board

③ WS-WD Recorder

④ NO-NO_2-NO_x Analyzer and Recorder

⑤ O_3 Analyzer and Recorder

⑥ Hydrocarbon Analyzer and Recorder

⑦ Space for RTI Calibration Assembly

⑧ Space for Other Instruments

⑨ Clean Air Supply (concealed beneath bench)

⑩ Electric Panel

⑪ Exhaust Manifold; Electric Power Strip

⑫ Heating System (air conditioner is mounted on the ceiling)

⑬ Compressed Gas Tanks (Outside)

⑭ Telephone

Figure 16. Interior plan view of mobile laboratory at Lewisburg, West Virginia.

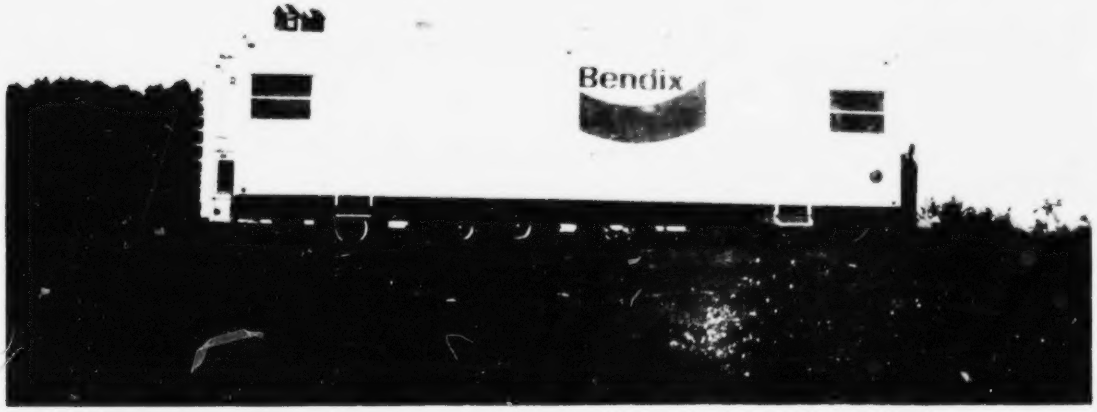


Figure 17. Exterior view of Lewisburg, West Virginia station.

4.2 Instrumentation

The instruments used to obtain measurements of air quality and meteorological parameters are described below. Parameters measured at each station are summarized in Table 1. In addition, wind speed and wind direction were monitored at McHenry, Maryland and Lewisburg, West Virginia.

Ambient ozone concentrations were measured at three of the stations using the Bendix Model 8002 Chemiluminescent Ozone Analyzer, while a McMillan Corporation MEC 1100 Chemiluminescent Ozone Analyzer was used at the Kane, Pennsylvania station. Nitrogen dioxide was measured at the three stations identified in Table 1 using the Bendix Model 8101B Chemiluminescent NO, NO_2, NO_x Analyzer. Nonmethane hydrocarbon concentrations were determined at the three stations identified in Table 1 using the Bendix Model 8201 Ambient Hydrocarbon Analyzer.

Table 1. PARAMETERS MEASURED AT MONITORING STATIONS

Station	Parameters
McHenry, Maryland	O_3, windspeed and direction
Kane, Pennsylvania	O_3, NO_2, NMHC
Coshocton, Ohio	O_3, NO_2, NMHC
Lewisburg, West Virginia	O_3, NO_2, NMHC, windspeed and direction

An air sampling system consisting of a 2.5-cm I.D. Teflon inlet line, a glass manifold with sampling ports, and a blower arrangement (to aspirate sample air from outside the shelter through the manifold system) was used at each station. An inverted glass funnel was used as an inlet to prevent moisture and settleable particulates from entering the system. Each analyzer sampled air drawn from the inlet manifold through a 5-μm porosity Teflon filter with Teflon filter element* and Teflon tubing.

Wind speed and wind direction were measured at two sites with a Climet Model 013-6 Wind System. The wind speed and wind direction transmitters were mounted on 9.2-m, guyed towers.

4.3 Instrument Calibration and Maintenance

4.3.1 Logistical Considerations

Dynamic calibration techniques were used to calibrate each analyzer at two-week intervals during the measurement period. Data obtained from the calibrations were used to provide updated transfer equations for converting voltage output to the physical units, micrograms per cubic meter.

The logistical problem of calibration and maintenance of ten instruments at four widely separated locations was approached as follows. Cylinders containing known concentrations of nitric oxide and methane were carried to each site requiring them and left for the duration of the study. A collection of items necessary to calibrate the instruments was assembled and packed such that it could be carried in a small, charter airplane.

4.3.2 Specific Calibration Techniques

Table 2 summarizes the calibration techniques for the pollutants monitored.

4.3.2.1 Calibration of Chemiluminescent Ozone Detector. Dynamic calibration of the ozone analyzers was achieved by use of an ultraviolet ozone generator. The ozone source consists of a shielded mercury vapor lamp (20.3-cm in length) which irradiates clean (compressed) air flowing through a 1.6-cm diameter quartz tube at a rate of 5 liters/minute. Variable ozone concentrations (0-1 ppm) can be generated by variable

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*As specified in 40 CFR 50, Appendix D.

Table 2. CALIBRATION TECHNIQUES

Pollutant	Technique
Ozone	Ultraviolet ozone generator referenced to neutral-buffered potassium iodide
Nitric oxide/nitrogen dioxide	Nitric oxide-ozone conversion unit
Nonmethane hydrocarbons	Standard calibration gas certified as to CH_4 content

shielding of the lamp envelope. As a reference method, the neutral-buffered potassium iodide (KI) technique was used. The concentration of ozone at each calibration point was verified by the KI method.

4.3.2.2 Calibration of Chemiluminescent NO-NO_2-NO_x Detector. The gas-phase titration technique developed by Hodgeson and associates at EPA[8] was used for the dynamic calibration of the NO, NO_x, NO_2 analyzer. The technique is based on the rapid gas-phase reaction between NO and O_3 which produces a stoichiometric quantity of NO_2. Nitric oxide (~50 ppm) in nitrogen (N_2) is diluted with zero air to provide NO concentrations in the range 0.01 to 0.50 ppm and used to calibrate the NO and NO_x channels. Nitrogen dioxide concentrations (0.01 to 0.50 ppm) are produced by the quantitative reaction of ozone with NO.

4.3.2.3 Calibration of Nonmethane Hydrocarbon Flame Ionization Detector. Calibration of the hydrocarbon analyzer was accomplished using mixtures of stable gases prepared to exact concentration in pressurized cylinders. Mixtures of methane in air purchased from Scott Research Laboratories with a certificate of analysis as to the methane concentration were used for all calibrations.

A detailed discussion of calibration methods and procedures is given in Appendix A.

4.3.3 Maintenance of Air Pollution Monitors

Maintenance of the automated instruments took place during the regularly scheduled biweekly calibration trips. Thus, no alterations affecting the response of the instrument (as may be caused by maintenance) occurred between calibration periods other than normal drift or analyzer failure. Specific maintenance included renewal of chart paper, ink, and magnetic tape, changing the 5-μm porosity Teflon filter element on the inlet line of each instrument, adjusting sample flow rate and reactant flow rates to those specified by the instrument manufacturer, and adjusting temperature controls such that the ideal room temperature of 298K was maintained as nearly as possible.

When failures occurred, the instrument was brought back on line as soon as possible. Specific failure time spans and reasons are summarized in Appendix B, "Performance Characteristics and Operational Summaries for Instruments."

4.4 Data Acquisition System

The magnetic tape data acquisition system used was the Westinghouse Pulse-o-Matic recording system which provided 15-minute integrated concentrations. A battery backup unit is included in the recorder to preserve the time information on tape in the event of a power failure. A photograph of one of the data acquisition systems is shown in Figure 18. Each of the small weather-tight enclosures contains a one pulse transmitter. The larger box contains the recording unit and battery backup components.

The tapes were replaced biweekly and returned to the Westinghouse Electric Corporation, Meter Division, Raleigh, North Carolina for translation to a form compatible with the RTI computer facility.

4.5 Data Reduction and Preliminary Processing

The data manipulation necessary to recover the data stored on a magnetic tape consisted of two phases:

1) translation of the tape to a form compatible with available data processing equipment, and
2) processing the data on a computer to obtain concentrations in $\mu g/m^3$.

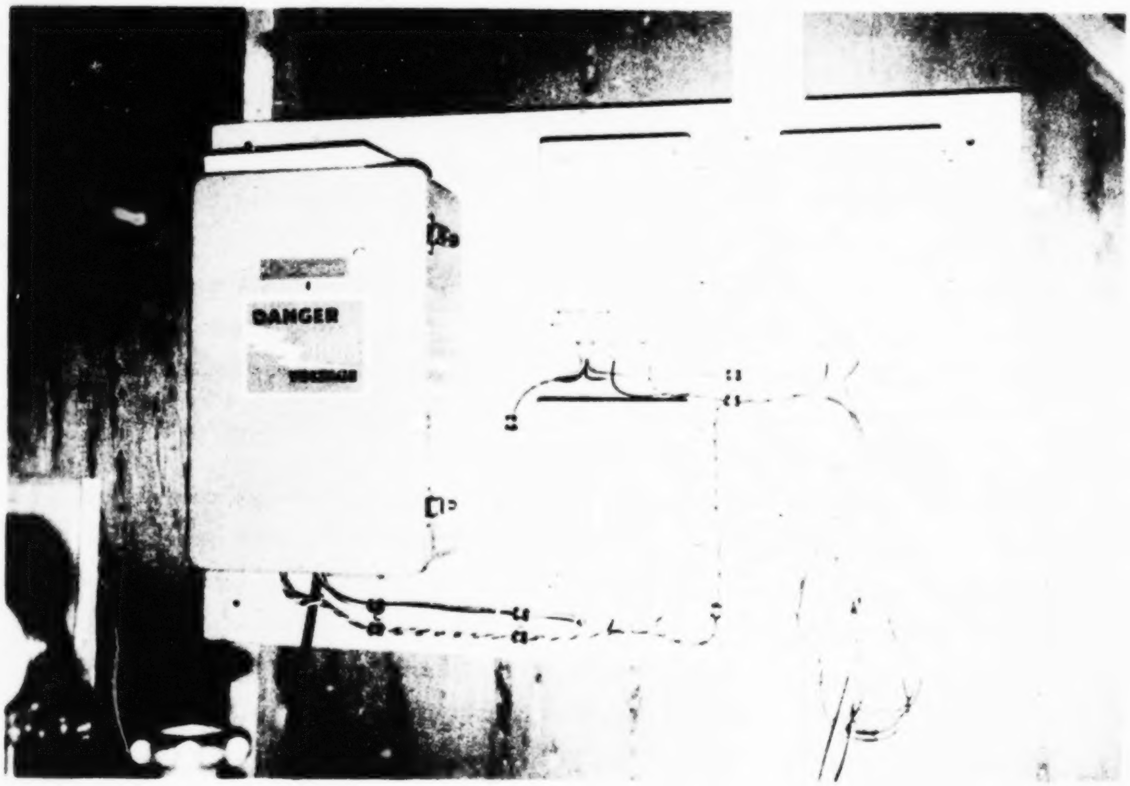

Figure 18. Data acquisition system.

The tape translation was done by the Meter Division, Westinghouse Electric Corporation. In their process, the tape is rewound and the pulses counted between each time mark. From information supplied by the user, including start and stop times, and times of any power failures, the actual date and time for each interval was computed. This information, both pulse counts and corresponding times, was printed out in tabular form and punched on IBM compatible cards for further processing. The data at this stage of processing were in the form of counts and had to be divided by 1500 to determine the average voltages.

The second phase consisted of processing the data on a computer to produce a printout for visual examination and a magnetic tape for use in the subsequent analysis of the data. In order to produce a printout which contained all information within itself, certain supplementary data had to be supplied to the computer along with the pulse counts. These data include times when the instruments were inoperative or not functioning correctly and linear best-fit equations relating the voltage output of the instrument to the concentration of the pollutant being measured. The times for instruments being inoperative came from operator logs, calibration notes, examination of preliminary computer runs, and strip charts. The equations were derived from data obtained during calibrations--the known input gas concentrations and the resulting voltage output from the instrument. A regression analysis was performed on these points to obtain a best-fit equation characterizing the instrument's response. The printout produced by the computer then contained the data in $\mu g/m^3$. If data were absent or invalid the number 99999 and a code letter were inserted to indicate the reason for the loss of data. A sample page of printout is shown in Figure 19. The magnetic tape which has the data recorded in computer compatible form contains exactly the same data less extraneous headings and spaces.

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                           EASTERN UNITED STATES OZONE ANALYSIS
                            RTI NO. 43U848-2          8/24/73

                         CONCENTRATION IN MICROGRAMS PER CUBIC METER

          MCHENRY,MD.              KANE,PA.                       COSHOCTON,OHIO                    LEWISBURG,W.VA.

 TIME     OZONE       OZONE      NO2       NMHC      OZONE       NO2       NMHC *    OZONE       NO2        NMHC

 1200     186.        105.       11.       0.         95.        42.       0.      99999. C     90.      99999. C
 1215     199.        106.       11.       0.        115.        44.       0.      99999. C      4.      99999. C
 1230     199.        108.       11.       0.        134.        36.       0.      99999. C      1.      99999. C
 1245     196.        111.       10.       0.        129.        34.       0.      99999. C      4.      99999. C
AVERAGE   195.        107.       10.       0.        118.        39.       0.      99999. Q     25.      99999. Q

 1300     186.        111.       10.       0.        144.        32.       0.      99999. C      6.      99999. C
 1315     171.        115.       11.       0.        154.        29.       0.      99999. C       .      99999. C
 1330     170.        120.       10.       0.        152.        28.       0.      99999. C      1.      99999. C
 1345     181.        134.       11.       0.        124.        31.       0.      99999. C     13.      99999. C
AVERAGE   177.        120.       10.       0.        144.        30.       0.      99999. Q      5.      99999. Q

 1400     193.        137.       12.       0.        105.        34.       0.      99999. C      2.      99999. C
 1415     208.        140.       12.       0.        129.        35.       0.      99999. C      2.      99999. C
 1430     207.        142.       11.       0.        122.        30.       0.      99999. C     12.      99999. C
 1445     207.        142.       11.       0.        117.        32.       0.      99999. C      8.      99999. C
AVERAGE   204.        140.       11.       0.        118.        33.       0.      99999. Q      6.      99999. Q

 1500     203.        142.       12.       0.        105.        32.       0.      99999. C      4.      99999. C
 1515     203.        146.       13.       0.        102.        31.       0.      99999. C      7.      99999. C
 1530     202.        145.       11.       0.         92.        31.       0.      99999. C      5.      99999. C
 1545     199.        142.       11.       0.         87.        31.       0.      99999. C      5.      99999. C
AVERAGE   202.        144.       12.       0.         97.        31.       0.      99999. Q      5.      99999. Q

 1600     203.        145.       11.       0.         82.        30.       0.        234.     99999. C  99999. C
 1615     199.        157.       12.       0.         95.        30.       0.        232.     99999. C  99999. C
 1630     179.        157.       11.       0.         92.        30.       0.        210.     99999. C  99999. C
 1645     175.        146.       11        0.         95.        30.       0.        228.     99999. C  99999. C
AVERAGE   189.        151.       11.       0.         91.        30.       0.        226.     99999. Q  99999. Q

 1700     181.        140.       12.       0.        100.        30.       0.        222.     99999. C      0.
 1715     182.        141.       11.       0.        100.        29.       0.        219.     99999. C      0.
 1730     179.        142.       12.       0.        107.        29.       0.        206.     99999. C      0.
 1745     174.        129.       18.       0.        102.        30.       0.        198.     99999. C      0.
AVERAGE   179.        138.       13.       0.        102.        30.       0.        211.     99999. Q      0.


     A ZERO POINT                 N INSTRUMENT NOT INSTALLED     Q INSUFFICIENT DATA
     C BEING CALIBRATED           P POWER FAILURE                X EQUIPMENT FAILURE
     K NO CALIBRATION DATA        O NMHC DATA INVALIDATED
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Figure 19. Sample page of printout of pollutant concentrations.

5.0 RESULTS

The results of the field measurement program are presented herein, with both primary and supplementary data included. Summary statistics, diurnal pollutant concentration patterns, and correlation coefficients, as appropriate, are presented below.

5.1 Primary Data (June 26-September 30, 1973)

5.1.1 Summary Statistics

Mean hourly ozone concentrations, standard deviations, and case counts by station are shown in Table 3; the corresponding statistics for nitrogen dioxide are given in Table 4. During this period 946, 1118, and 1334 determinations of hourly nonmethane hydrocarbon concentrations were made at Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia, respectively. These observations were discarded when it was learned that the hydrocarbon analyzers used were affected by water vapor, thus giving erroneously high nonmethane hydrocarbon concentrations.*

Cumulative frequency distributions for hourly pollutant concentrations for the entire period are presented in Table 5. Maximum hourly ozone concentrations (concentration exceeded during approximately one percent of hours) were 320 μg/m^3 at McHenry, Maryland; 270 μg/m^3 at Kane, Pennsylvania; 340 μg/m^3 at Coshocton, Ohio; and 250 μg/m^3 at Lewisburg, West Virginia.

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*During the field measurement program, RTI chemists became suspicious of the high nonmethane hydrocarbon concentrations being determined with the Bendix instrument. Their suspicions were confirmed by the quality assurance program (described elsewhere in this volume) which indicated that the nonmethane hydrocarbon concentrations determined with the Bendix instrument were indeed high when compared with simultaneous determinations made with the Beckman Model 6800 Gas Chromatographic Flame Ionization Detector. At the request of RTI, Bendix Corporation personnel investigated the problem and determined that total hydrocarbon measurements made with their analyzer were subject to a positive moisture interference. Hence, nonmethane hydrocarbon concentrations obtained by subtracting the methane concentration from the total hydrocarbon concentration were erroneously high. Since the moisture interference was not defined quantitatively, there was no basis for adjusting and thereby recovering earlier nonmethane hydrocarbon concentration determinations. Bendix Corporation modified the analyzer at the Kane, Pennsylvania station in mid-October by adding a column to remove water vapor from the air steam used for the total hydrocarbon concentration measurement. Subsequent measurements at Kane, Pennsylvania were considered valid.

Table 3. STATISTICAL SUMMARY OF HOURLY OZONE CONCENTRATION MEASUREMENTS BY STATION
June 26-September 30, 1973

Station	Mean hourly concentration ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Case count
McHenry, Maryland	148.9	56.0	1,622
Kane, Pennsylvania	130.3	56.8	2,131
Coshocton, Ohio	111.5	62.7	1,785
Lewisburg, West Virginia	105.4	53.5	1,663

Table 4. STATISTICAL SUMMARY OF HOURLY NITROGEN DIOXIDE CONCENTRATION MEASUREMENTS BY STATION
June 26-September 30, 1973

Station	Mean hourly concentration ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Case count
Kane, Pennsylvania	11.3	8.0	1,869
Coshocton, Ohio	21.4	15.4	2,043
Lewisburg, West Virginia	16.3	14.6	1,699

Tables 5a,b,c, and d show the cumulative frequency distributions for hourly pollutant concentrations for June, July, August, and September, respectively. The frequency distributions of hourly ozone concentrations by month are plotted in Figures 20, 21, 22, and 23 for McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia, respectively.

The mean hourly ozone concentrations shown in Table 3 can be compared with the 112 $\mu g/m^3$ mean hourly concentration observed during the

(Text continued on page 1-46)

Table 5. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (June 26 - September 30, 1973)

	Percent of samples greater than stated concentration									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Concentration ($\mu g/m^3$)	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
0.	100.0	100.0	97.6	0.0	100.0	99.9	0.0	100.0	98.4	0.0
10.	100.0	100.0	52.6	0.0	99.6	68.8	0.0	99.9	58.4	0.0
20.	100.0	99.8	11.1	0.0	97.6	51.1	0.0	98.7	24.1	0.0
30.	99.4	99.2	2.5	0.0	93.9	26.0	0.0	95.3	17.1	0.0
40.	98.6	98.0	.6	0.0	89.2	10.6	0.0	90.3	14.1	0.0
50.	97.3	94.6	.1	0.0	83.2	4.3	0.0	84.3	1.8	0.0
60.	95.4	90.9	.1	0.0	77.2	1.6	0.0	76.7	.6	0.0
70.	93.8	85.5	.1	0.0	71.8	.8	0.0	69.3	.1	0.0
80.	91.5	79.2	.1	0.0	65.1	.4	0.0	62.7	.1	0.0
90.	88.5	71.9	.1	0.0	56.8	.1	0.0	55.4	.1	0.0
100.	83.7	64.9	0.0	0.0	52.5	.1	0.0	50.4	.1	0.0
110.	77.2	59.2	0.0	0.0	46.7	.1	0.0	44.9	.1	0.0
120.	69.2	52.1	0.0	0.0	39.7	.0	0.0	37.7	.1	0.0
130.	60.7	45.8	0.0	0.0	34.4	0.0	0.0	30.8	.1	0.0
140.	53.0	39.0	0.0	0.0	28.7	0.0	0.0	23.5	.1	0.0
150.	44.7	33.8	0.0	0.0	24.5	0.0	0.0	18.3	.1	0.0
160.	36.9	29.8	0.0	0.0	19.6	0.0	0.0	15.2	.1	0.0
170.	29.8	24.7	0.0	0.0	15.7	0.0	0.0	12.9	0.0	0.0
180.	24.2	20.7	0.0	0.0	12.0	0.0	0.0	10.3	0.0	0.0
190.	19.6	16.5	0.0	0.0	9.3	0.0	0.0	8.2	0.0	0.0
200.	16.0	12.9	0.0	0.0	7.3	0.0	0.0	6.1	0.0	0.0
210.	12.6	10.4	0.0	0.0	5.6	0.0	0.0	4.3	0.0	0.0
220.	9.4	7.8	0.0	0.0	4.2	0.0	0.0	3.0	0.0	0.0
230.	7.6	5.6	0.0	0.0	3.9	0.0	0.0	2.1	0.0	0.0
240.	6.2	4.1	0.0	0.0	3.5	0.0	0.0	1.6	0.0	0.0
250.	4.9	2.7	0.0	0.0	3.2	0.0	0.0	.9	0.0	0.0
260.	4.4	1.6	0.0	0.0	2.9	0.0	0.0	.7	0.0	0.0
270.	3.9	.9	0.0	0.0	2.2	0.0	0.0	.2	0.0	0.0
280.	3.0	.7	0.0	0.0	2.0	0.0	0.0	.1	0.0	0.0
290.	2.2	.4	0.0	0.0	1.9	0.0	0.0	0.0	0.0	0.0
300.	1.6	.2	0.0	0.0	1.6	0.0	0.0	0.0	0.0	0.0
310.	1.3	.1	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0
320.	1.0	.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0
330.	.8	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0
340.	.5	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0
350.	.4	0.0	0.0	0.0	.8	0.0	0.0	0.0	0.0	0.0
360.	.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
370.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
380.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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*Nonmethane hydrocarbon data invalid

Table 5a. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (June 26 - June 30, 1973)

	Percent of samples greater than stated concentration									
	McHenry	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Concentration ($\mu g/m^3$)	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
0.	0.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.	0.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
20.	0.0	100.0	94.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30.	0.0	100.0	36.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
40.	0.0	100.0	5.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
50.	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
60.	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
70.	0.0	89.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
80.	0.0	79.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
90.	0.0	73.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
100.	0.0	65.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
110.	0.0	57.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
120.	0.0	51.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
130.	0.0	40.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
140.	0.0	38.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
150.	0.0	32.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
160.	0.0	30.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
170.	0.0	24.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
180.	0.0	14.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
190.	0.0	4.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
200.	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
210.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
220.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
230.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
240.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
250.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
260.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
270.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
280.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
290.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
300.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
310.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
320.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
330.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
340.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
350.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
360.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
370.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
380.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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*Nonmethane hydrocarbon data invalid

Table 5b. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (July 1-July 31, 1973)

	Percent of samples greater than stated concentration									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Concentration (μg/m^3)	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
	100.0	100.0	100.0	0.0	100.0	100.0	0.0	100.0	100.0	0.0
0.	100.0	100.0	100.0	0.0	100.0	99.8	0.0	100.0	94.2	0.0
10.	100.0	100.0	47.1	0.0	99.1	56.7	0.0	100.0	41.2	0.0
20.	100.0	100.0	7.1	0.0	96.8	40.1	0.0	97.8	14.6	0.0
30.	100.0	100.0	1.3	0.0	94.0	29.5	0.0	93.4	3.6	0.0
40.	100.0	99.5	.6	0.0	90.6	11.6	0.0	87.0	.8	0.0
50.	100.0	97.9	0.0	0.0	85.5	4.2	0.0	82.0	0.0	0.0
60.	100.0	95.2	0.0	0.0	78.6	1.3	0.0	75.7	0.0	0.0
70.	100.0	90.6	0.0	0.0	72.2	.5	0.0	69.3	0.0	0.0
80.	100.0	84.3	0.0	0.0	65.3	0.0	0.0	63.0	0.0	0.0
90.	99.4	75.5	0.0	0.0	58.6	0.0	0.0	53.3	0.0	0.0
100.	97.7	67.3	0.0	0.0	51.5	0.0	0.0	47.8	0.0	0.0
110.	93.1	58.0	0.0	0.0	46.0	0.0	0.0	41.7	0.0	0.0
120.	81.6	51.1	0.0	0.0	39.5	0.0	0.0	30.4	0.0	0.0
130.	68.4	45.5	0.0	0.0	36.8	0.0	0.0	19.1	0.0	0.0
140.	60.3	37.5	0.0	0.0	31.5	0.0	0.0	8.6	0.0	0.0
150.	44.3	34.2	0.0	0.0	26.5	0.0	0.0	4.1	0.0	0.0
160.	31.0	29.7	0.0	0.0	23.4	0.0	0.0	2.8	0.0	0.0
170.	21.3	24.4	0.0	0.0	20.7	0.0	0.0	2.5	0.0	0.0
180.	13.2	21.0	0.0	0.0	16.6	0.0	0.0	.8	0.0	0.0
190.	10.9	16.2	0.0	0.0	12.9	0.0	0.0	0.0	0.0	0.0
200.	9.2	12.0	0.0	0.0	9.9	0.0	0.0	0.0	0.0	0.0
210.	6.9	9.5	0.0	0.0	6.7	0.0	0.0	0.0	0.0	0.0
220.	4.0	6.0	0.0	0.0	4.1	0.0	0.0	0.0	0.0	0.0
230.	2.3	3.4	0.0	0.0	3.4	0.0	0.0	0.0	0.0	0.0
240.	2.3	1.8	0.0	0.0	2.8	0.0	0.0	0.0	0.0	0.0
250.	.6	.8	0.0	0.0	2.3	0.0	0.0	0.0	0.0	0.0
260.	0.0	.1	0.0	0.0	1.6	0.0	0.0	0.0	0.0	0.0
270.	0.0	0.0	0.0	0.0	.2	0.0	0.0	0.0	0.0	0.0
280.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
290.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
300.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
310.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
320.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
330.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
340.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
350.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	[illegible]
360.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	[illegible]
370.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	[illegible]
380.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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*Nonmethane hydrocarbon data invalid

Table 5c. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (August 1-August 31, 1973)

	Percent of samples greater than stated concentration									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Concentration (µg/m³)	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
0.	100.0	100.0	100.0	0.0	100.0	99.9	0.0	100.0	99.0	0.0
10.	100.0	100.0	60.2	0.0	99.9	48.9	0.0	100.0	48.9	0.0
20.	100.0	100.0	10.9	0.0	96.4	32.7	0.0	98.5	9.0	0.0
30.	99.2	99.3	2.8	0.0	94.7	13.2	0.0	95.0	1.9	0.0
40.	98.5	98.9	.7	0.0	89.9	5.3	0.0	89.2	1.0	0.0
50.	98.4	98.5	.3	0.0	84.3	3.1	0.0	83.4	.5	0.0
60.	98.2	97.3	.1	0.0	78.4	1.2	0.0	75.8	.3	0.0
70.	98.1	95.6	.1	0.0	73.5	.8	0.0	69.2	.2	0.0
80.	97.7	91.4	.1	0.0	66.1	.5	0.0	63.4	.2	0.0
90.	95.1	85.9	.1	0.0	63.2	.4	0.0	57.5	.2	0.0
100.	90.1	80.9	0.0	0.0	57.0	.4	0.0	54.5	.2	0.0
110.	83.4	77.4	0.0	0.0	51.6	.3	0.0	49.2	.2	0.0
120.	75.3	72.4	0.0	0.0	44.1	.1	0.0	42.5	.2	0.0
130.	65.1	64.7	0.0	0.0	38.5	0.0	0.0	37.3	.2	0.0
140.	58.4	56.2	0.0	0.0	33.0	0.0	0.0	32.6	.2	0.0
150.	52.2	50.5	0.0	0.0	28.4	0.0	0.0	27.2	.2	0.0
160.	45.5	45.2	0.0	0.0	23.1	0.0	0.0	23.4	.2	0.0
170.	39.4	39.0	0.0	0.0	18.6	0.0	0.0	21.3	0.0	0.0
180.	32.3	33.8	0.0	0.0	13.9	0.0	0.0	18.0	0.0	0.0
190.	26.8	27.7	0.0	0.0	11.5	0.0	0.0	15.3	0.0	0.0
200.	23.2	22.9	0.0	0.0	9.5	0.0	0.0	12.4	0.0	0.0
210.	18.6	19.6	0.0	0.0	7.9	0.0	0.0	8.7	0.0	0.0
220.	14.1	15.7	0.0	0.0	7.2	0.0	0.0	5.9	0.0	0.0
230.	11.8	12.7	0.0	0.0	7.0	0.0	0.0	4.2	0.0	0.0
240.	10.1	10.2	0.0	0.0	6.7	0.0	0.0	3.5	0.0	0.0
250.	8.4	7.1	0.0	0.0	6.4	0.0	0.0	2.0	0.0	0.0
260.	7.6	4.6	0.0	0.0	6.0	0.0	0.0	1.3	0.0	0.0
270.	6.8	2.7	0.0	0.0	5.3	0.0	0.0	.2	0.0	0.0
280.	5.2	1.9	0.0	0.0	4.9	0.0	0.0	0.0	0.0	0.0
290.	4.2	1.1	0.0	0.0	4.6	0.0	0.0	0.0	0.0	0.0
300.	3.1	.7	0.0	0.0	4.0	0.0	0.0	0.0	0.0	0.0
310.	2.4	.4	0.0	0.0	3.3	0.0	0.0	0.0	0.0	0.0
320.	1.9	.1	0.0	0.0	3.1	0.0	0.0	0.0	0.0	0.0
330.	1.5	0.0	0.0	0.0	2.7	0.0	0.0	0.0	0.0	0.0
340.	1.1	0.0	0.0	0.0	2.3	0.0	0.0	0.0	0.0	0.0
350.	.8	0.0	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0
360.	.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
370.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
380.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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*Nonmethane hydrocarbon data invalid

Table 5d. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (September 1-September 30, 1973)

Percent of samples greater than stated concentration

Concentration (µg/m³)	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
0.	100.0	100.0	93.1	0.0	100.0	100.0	0.0	100.0	100.0	0.0
10.	100.0	99.8	46.6	0.0	99.7	99.3	0.0	99.9	75.4	0.0
20.	100.0	99.3	13.6	0.0	97.2	79.0	0.0	99.3	41.9	0.0
30.	99.4	98.2	2.8	0.0	92.9	36.4	0.0	95.9	37.2	0.0
40.	98.5	95.0	.5	0.0	87.5	15.2	0.0	92.9	32.3	0.0
50.	95.5	86.0	0.0	0.0	80.4	5.5	0.0	86.3	3.9	0.0
60.	91.3	78.4	0.0	0.0	74.7	2.2	0.0	77.9	1.1	0.0
70.	87.8	69.0	0.0	0.0	69.5	1.0	0.0	69.6	.1	0.0
80.	83.0	59.0	0.0	0.0	61.4	.7	0.0	62.0	0.0	0.0
90.	78.9	51.5	0.0	0.0	53.8	0.0	0.0	54.8	0.0	0.0
100.	73.7	43.7	0.0	0.0	47.6	0.0	0.0	48.3	0.0	0.0
110.	66.9	36.3	0.0	0.0	41.3	0.0	0.0	42.8	0.0	0.0
120.	59.8	30.1	0.0	0.0	34.5	0.0	0.0	37.4	0.0	0.0
130.	54.4	24.4	0.0	0.0	27.9	0.0	0.0	31.3	0.0	0.0
140.	45.6	18.4	0.0	0.0	21.7	0.0	0.0	23.5	0.0	0.0
150.	37.1	13.8	0.0	0.0	17.0	0.0	0.0	18.0	0.0	0.0
160.	29.5	11.9	0.0	0.0	12.8	0.0	0.0	14.6	0.0	0.0
170.	23.1	8.9	0.0	0.0	8.9	0.0	0.0	11.0	0.0	0.0
180.	18.5	6.0	0.0	0.0	6.6	0.0	0.0	8.6	0.0	0.0
190.	14.3	4.7	0.0	0.0	4.2	0.0	0.0	6.5	0.0	0.0
200.	10.1	3.1	0.0	0.0	2.8	0.0	0.0	4.0	0.0	0.0
210.	7.7	2.6	0.0	0.0	2.1	0.0	0.0	2.7	0.0	0.0
220.	5.8	1.3	0.0	0.0	.6	0.0	0.0	2.1	0.0	0.0
230.	4.5	.3	0.0	0.0	.5	0.0	0.0	1.4	0.0	0.0
240.	3.1	0.0	0.0	0.0	.3	0.0	0.0	.8	0.0	0.0
250.	2.4	0.0	0.0	0.0	0.0	0.0	0.0	.4	0.0	0.0
260.	2.2	0.0	0.0	0.0	0.0	0.0	0.0	.4	0.0	0.0
270.	1.6	0.0	0.0	0.0	0.0	0.0	0.0	.3	0.0	0.0
280.	1.4	0.0	0.0	0.0	0.0	0.0	0.0	.1	0.0	0.0
290.	.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
300.	.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
310.	.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
320.	.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
330.	.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
340.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
350.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
360.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
370.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
380.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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*Nonmethane hydrocarbon data invalid

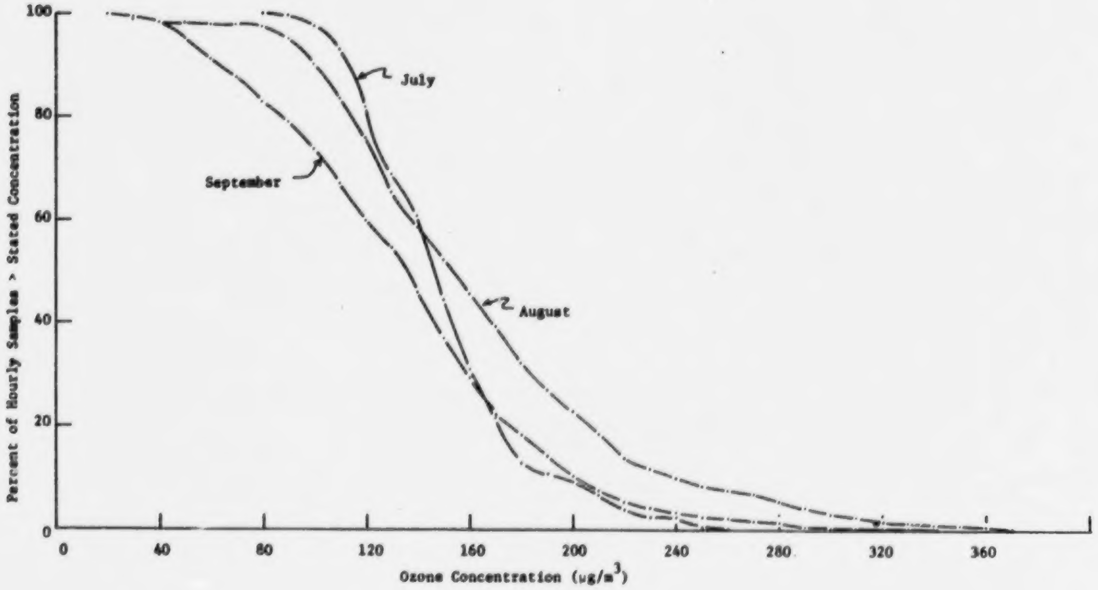

Figure 20. Frequency distribution of hourly ozone concentrations for July, August, and September, 1973, at McHenry, Maryland.

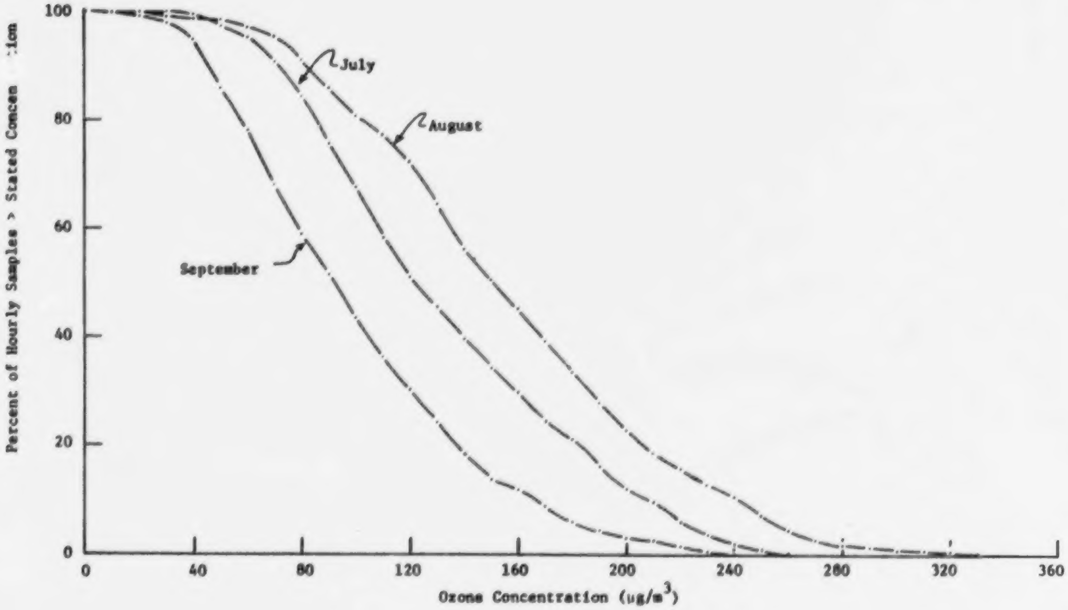

Figure 21. Frequency distributions of hourly ozone concentrations for July, August, and September, 1973, at Kane Pennsylvania.

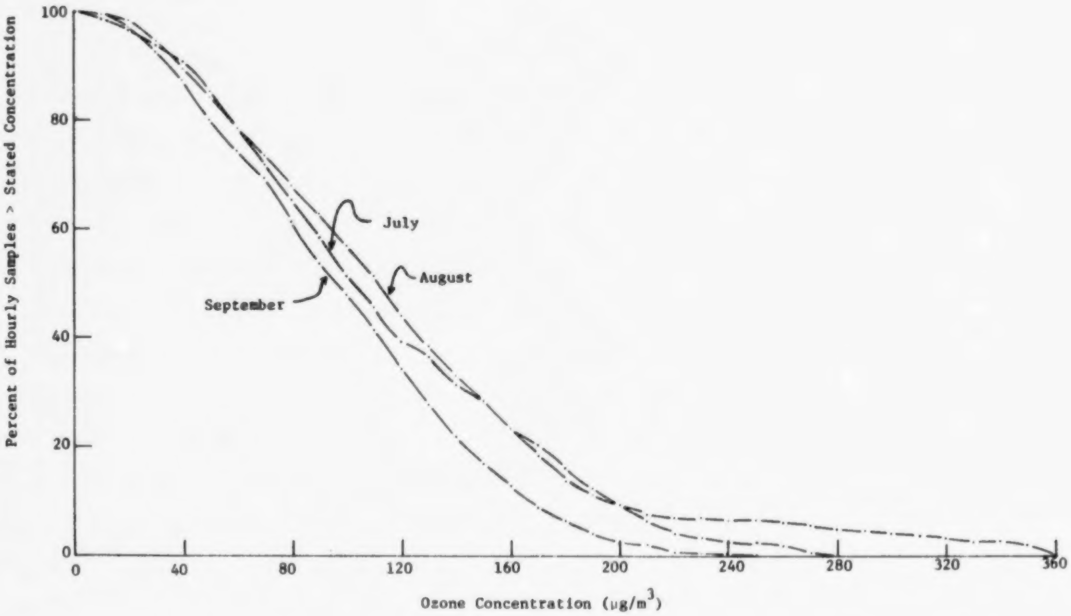

Figure 22. Frequency distributions of hourly ozone concentration for July, August, and September, 1973, at Coshocton, Ohio

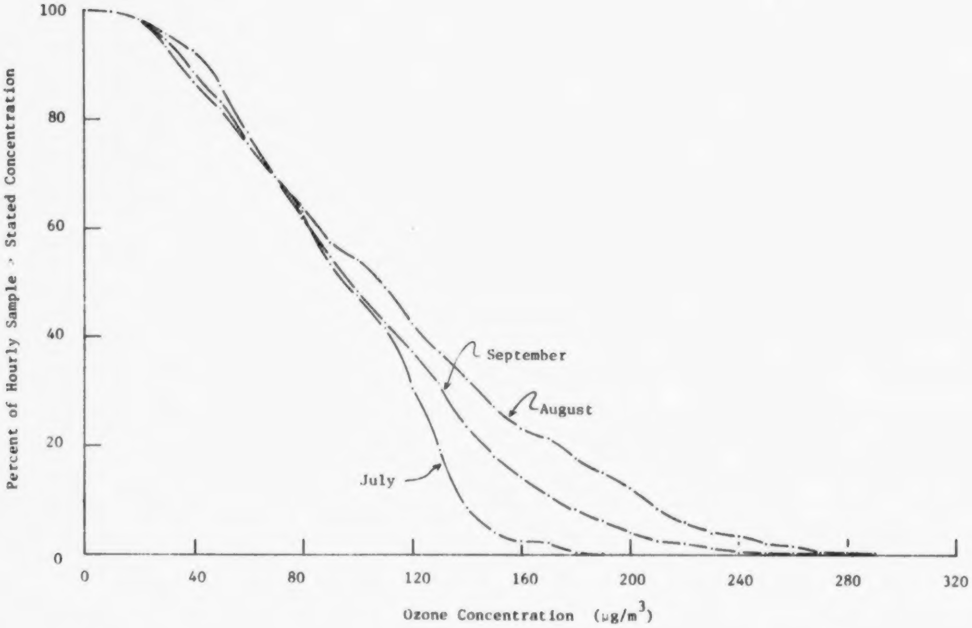

Figure 23. Frequency distributions of hourly ozone concentration for July, August, and September, 1973, at Lewisburg, West Virginia

period August 4 to September 25, 1972 at McHenry, Maryland. Similarly the hourly nitrogen dioxide concentrations given in Table 4 can be compared with the 14 $\mu g/m^3$ mean hourly concentration for August 4 to September 25, 1972 at McHenry, Maryland. The NAAQS for photochemical oxidants (160 $\mu g/m^3$) was exceeded during approximately 37, 30, 20, and 15 percent of the hours at McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia. In contrast, the NAAQS for photochemical oxidants was exceeded at McHenry, Maryland during approximately 11 percent of the hours between August 4 and September 25, 1972. At McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia the 160 $\mu g/m^3$ hourly ozone concentration was exceeded on 78, 65, 46, and 39 percent, respectively, of the days for which data are available during 1973. On the basis of the data presented in Table 4, it is unlikely that the NAAQS for nitrogen dioxide (100 $\mu g/m^3$) as an annual arithmetic mean would be exceeded at any of the three locations.

5.1.2 Diurnal Patterns

Mean pollutant concentrations for each hour of the day are shown in Table 6 and mean diurnal curves of ozone and nitrogen dioxide concentrations are presented in Figures 24 and 25, respectively. While the diurnal patterns of ozone concentration generally followed that shown in Figure 24, marked departures from that from that pattern did occur. Thus, Figure 26 presents examples of daily ozone concentration peaking at night and selected episodes of persistent high (>160 $\mu g/m^3$) ozone concentration are depicted in Figure 27. Figure 28 contrasts the mean diurnal ozone concentration curves for 1972 and 1973 at McHenry, Maryland. In addition to higher concentrations, the 1973 curve exhibits a strong diurnal characteristic when contrasted with its 1972 counterpart.

Mean diurnal ozone concentration curves for three urban locations within the study area are presented for comparative purposes in Figure 29.

5.1.3 Correlations

Correlation coefficients for simultaneous hourly ozone concentration versus hourly nitrogen dioxide concentration within and between stations are presented in Table 7. Cross correlation coefficients

(Text continued on page 1-56)

Table 6. MEANS AND STANDARD DEVIATIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON FOR EACH HOUR OF THE DAY (June 26-September 30, 1973)

	Concentration ($\mu g/m^3$)									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Time(EDT) at beginning of sample	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
0100										
MEAN	141.3	119.4	12.9	0.0	103.4	21.5	0.0	82.4	17.1	0.0
STD DEV	47.8	42.8	7.6	0.0	52.3	14.7	0.0	32.2	13.6	0.0
CASES	68	90	77	40	75	84	47	71	71	56
0200										
MEAN	139.5	113.6	13.0	0.0	99.3	21.1	0.0	74.9	15.9	0.0
STD DEV	48.4	47.0	7.9	0.0	57.2	13.8	0.0	32.5	13.9	0.0
CASES	68	90	78	41	75	84	47	71	71	56
0300										
MEAN	137.0	109.5	12.0	0.0	96.0	22.4	0.0	66.9	14.7	0.0
STD DEV	45.5	44.3	6.8	0.0	56.7	14.6	0.0	31.2	13.9	0.0
CASES	68	90	78	41	75	84	47	71	71	56
0400										
MEAN	132.9	105.9	10.8	0.0	92.7	23.6	0.0	61.9	13.9	0.0
STD DEV	46.1	43.4	5.6	0.0	56.7	15.7	0.0	29.1	13.6	0.0
CASES	68	90	78	40	75	86	47	71	71	56
0500										
MEAN	127.7	102.6	10.8	0.0	76.4	24.2	0.0	60.0	13.6	0.0
STD DEV	47.7	42.2	6.3	0.0	56.2	16.3	0.0	31.6	13.3	0.0
CASES	68	90	79	40	75	86	47	71	71	56
0600										
MEAN	123.7	99.4	11.1	0.0	71.6	24.5	0.0	59.6	13.1	0.0
STD DEV	47.0	41.2	7.2	0.0	54.4	16.3	0.0	31.0	14.1	0.0
CASES	68	90	78	40	75	86	47	71	71	56
0700										
MEAN	118.2	95.2	12.3	0.0	65.5	25.[illegible]	0.0	56.0	13.3	0.0
STD DEV	45.6	42.3	7.9	0.0	55.7	17.4	0.0	29.7	14.3	0.0
CASES	68	90	78	40	75	86	47	71	71	56
0800										
MEAN	117.6	91.5	14.9	0.0	62.2	25.9	0.0	54.4	14.9	0.0
STD DEV	46.5	41.9	8.6	0.0	51.[illegible]	17.2	0.0	27.3	14.6	0.0
CASES	68	89	78	39	74	86	47	71	71	56

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* The 0.0 entry under Nonmethane hydrocarbon indicates invalid data; the case counts are included for information purposes.

Table 6 (cont'd). MEANS AND STANDARD DEVIATIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON FOR EACH HOUR OF THE DAY (June 26-September 30, 1973)

	Concentration ($\mu g/m^3$)									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Time(EDT) at beginning of sample	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
0900										
MEAN	117.3	92.2	15.4	0.0	62.7	25.2	0.0	53.2	16.0	0.0
STD DEV	44.2	39.9	8.4	0.0	45.0	15.8	0.0	27.6	15.0	0.0
CASES	58	96	77	38	74	84	47	70	71	56
1000										
MEAN	126.3	103.5	14.8	0.0	74.7	24.0	0.0	83.1	15.4	0.0
STD DEV	46.5	41.2	12.8	0.0	43.4	14.6	0.0	33.4	13.8	0.0
CASES	55	96	77	38	72	85	47	70	71	56
1100										
MEAN	138.7	125.9	12.0	0.0	95.6	27.4	0.0	107.8	16.3	0.0
STD DEV	47.2	49.4	7.7	0.0	48.5	15.1	0.0	36.9	14.9	0.0
CASES	58	85	75	37	72	85	47	68	69	55
1200										
MEAN	151.7	141.0	10.7	0.0	114.5	22.0	0.0	137.4	17.0	0.0
STD DEV	55.4	54.7	6.5	0.0	51.7	15.2	0.0	43.2	14.6	0.0
CASES	57	88	76	37	72	85	46	68	69	55
1300										
MEAN	153.4	149.7	9.5	0.0	125.2	22.2	0.0	147.3	15.8	0.0
STD DEV	57.9	53.9	5.5	0.0	56.2	17.7	0.0	46.8	13.7	0.0
CASES	56	90	76	38	72	84	45	67	68	54
1400										
MEAN	170.4	155.4	8.6	0.0	141.8	21.1	0.0	152.2	16.8	0.0
STD DEV	59.1	54.0	6.5	0.0	56.5	17.3	0.0	44.8	15.7	0.0
CASES	56	90	78	38	73	84	45	67	69	53
1500										
MEAN	178.6	161.4	7.8	0.0	147.9	21.3	0.0	152.5	17.6	0.0
STD DEV	52.9	54.5	6.9	0.0	56.2	19.5	0.0	43.4	16.1	0.0
CASES	56	90	78	37	74	83	45	66	69	53
1600										
MEAN	180.1	164.3	8.4	0.0	151.0	20.0	0.0	157.6	18.4	0.0
STD DEV	57.5	54.5	7.4	0.0	55.3	15.6	0.0	43.3	23.1	0.0
CASES	55	90	79	40	74	82	46	66	70	55

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* The 0.0 entry under Nonmethane hydrocarbon indicates invalid data; the case counts are included for information purposes.

Table 6 (cont'd). MEANS AND STANDARD DEVIATIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON FOR EACH HOUR OF THE DAY (June 26-September 30, 1973)

	Concentration ($\mu g/m^3$)									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Time(EDT) at beginning of sample	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
1700										
MEAN	179.6	163.1	7.6	0.0	155.4	19.1	0.0	158.8	15.8	0.0
STD DEV	57.8	56.0	7.2	0.0	55.5	13.1	0.0	46.5	13.2	0.0
CASES	66	91	80	40	75	82	46	58	70	56
1800										
MEAN	177.5	168.5	7.4	0.0	155.0	17.3	0.0	153.8	16.7	0.0
STD DEV	57.8	59.0	6.5	0.0	53.0	12.6	0.0	44.7	14.1	0.0
CASES	65	90	80	41	76	85	47	69	71	57
1900										
MEAN	174.3	164.7	8.1	0.0	152.0	16.8	0.0	146.6	16.0	0.0
STD DEV	57.0	59.0	6.6	0.0	54.7	12.9	0.0	42.3	13.6	0.0
CASES	68	90	79	41	76	85	47	72	73	56
2000										
MEAN	169.6	152.5	11.1	0.0	144.1	17.0	0.0	138.3	16.9	0.0
STD DEV	58.3	59.4	6.9	0.[illegible]	58.7	13.8	0.0	40.8	13.9	0.0
CASES	69	89	79	4[illegible]	76	86	47	72	73	56
2100										
MEAN	163.4	142.5	13.5	0.0	133.6	17.9	0.0	129.1	18.3	0.0
STD DEV	57.6	59.7	9.3	0.0	56.4	14.3	0.0	45.8	14.2	0.0
CASES	69	87	78	40	75	84	47	70	72	56
2200										
MEAN	157.3	137.8	13.5	0.0	128.5	18.5	0.0	118.6	19.2	0.0
STD DEV	55.4	57.9	8.4	0.0	54.6	13.4	0.0	46.0	13.4	0.0
CASES	69	85	78	40	75	84	46	70	72	56
2300										
MEAN	150.3	132.3	12.4	0.0	119.9	19.7	0.0	105.4	19.4	0.0
STD DEV	50.7	56.6	6.4	0.0	56.4	13.4	0.0	39.9	14.0	0.0
CASES	69	85	78	40	75	86	47	71	72	56
2400										
MEAN	143.9	124.8	14.0	0.0	112.1	20.8	0.0	92.0	18.8	0.0
STD DEV	48.5	53.1	6.8	0.0	56.2	14.1	0.0	35.8	13.8	0.0
CASES	69	89	78	40	75	87	47	71	72	56

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* The 0.0 entry under Nonmethane hydrocarbon indicates invalid data; the case counts are included for information purposes.

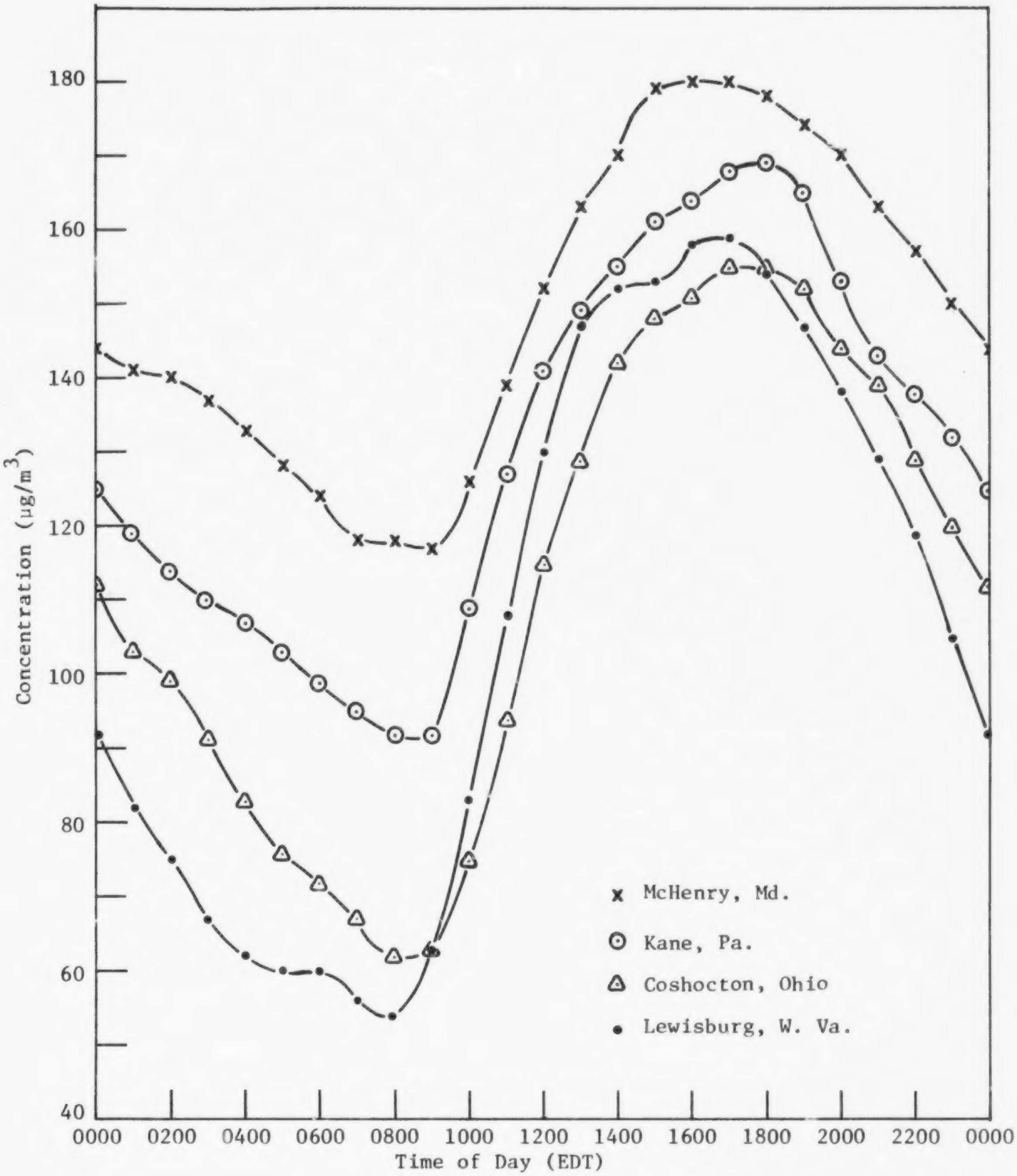


Figure 24. Mean diurnal ozone concentrations at McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia, from June 26 to September 30, 1973.

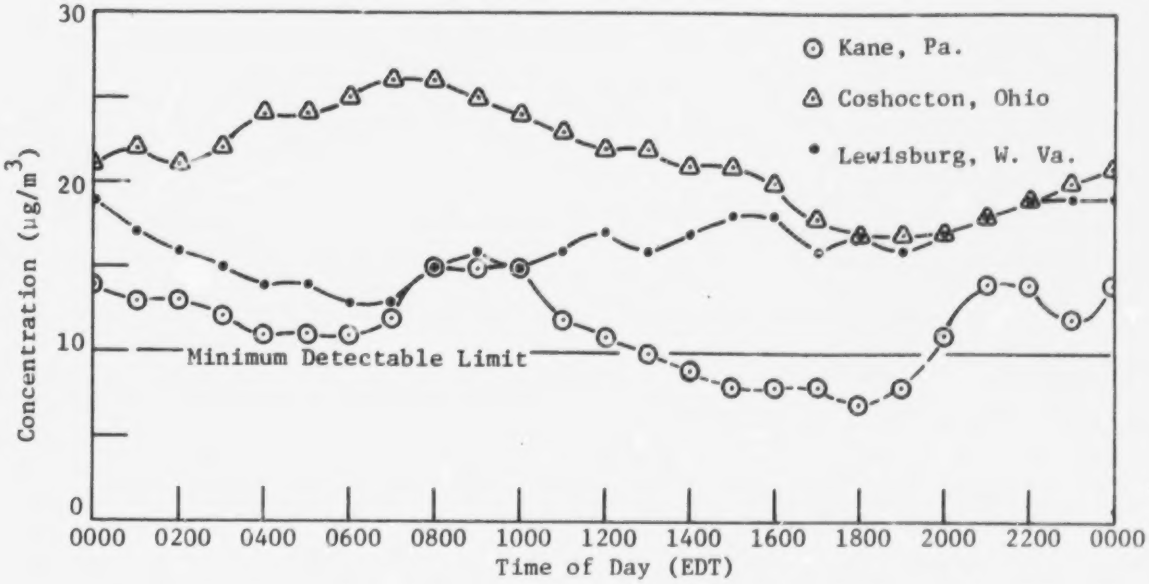


Figure 25. Mean diurnal nitrogen dioxide concentrations at Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia from June 26 to September 30, 1973.

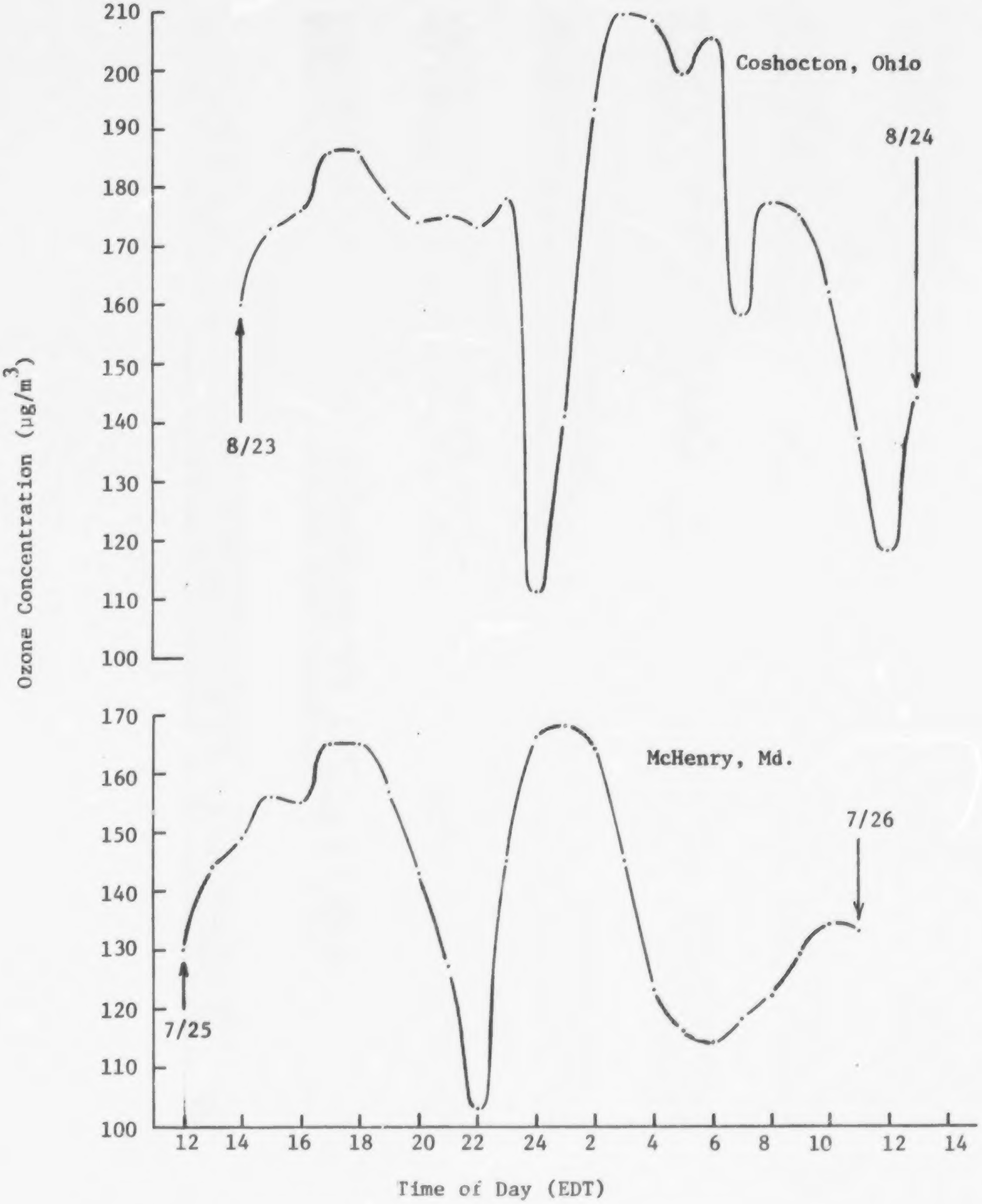


Figure 26. Examples of night-time ozone concentration maxima at McHenry, Maryland and Coshocton, Ohio during summer, 1973.

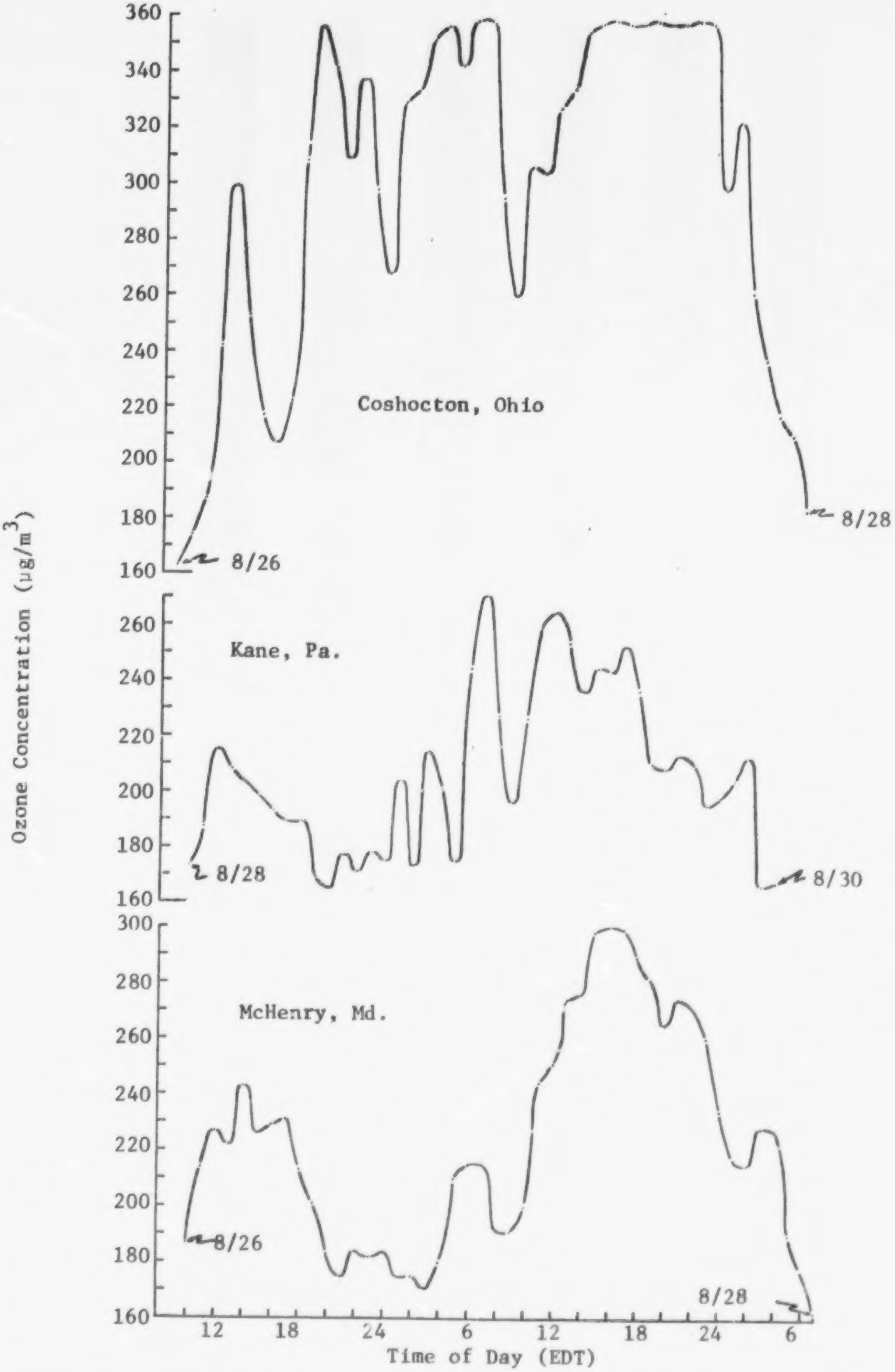


Figure 27. Selected episodes of high ozone concentration (>160 μg/m³) at McHenry, Maryland; Kane, Pennsylvania; and Coshocton, Ohio during August, 1973.

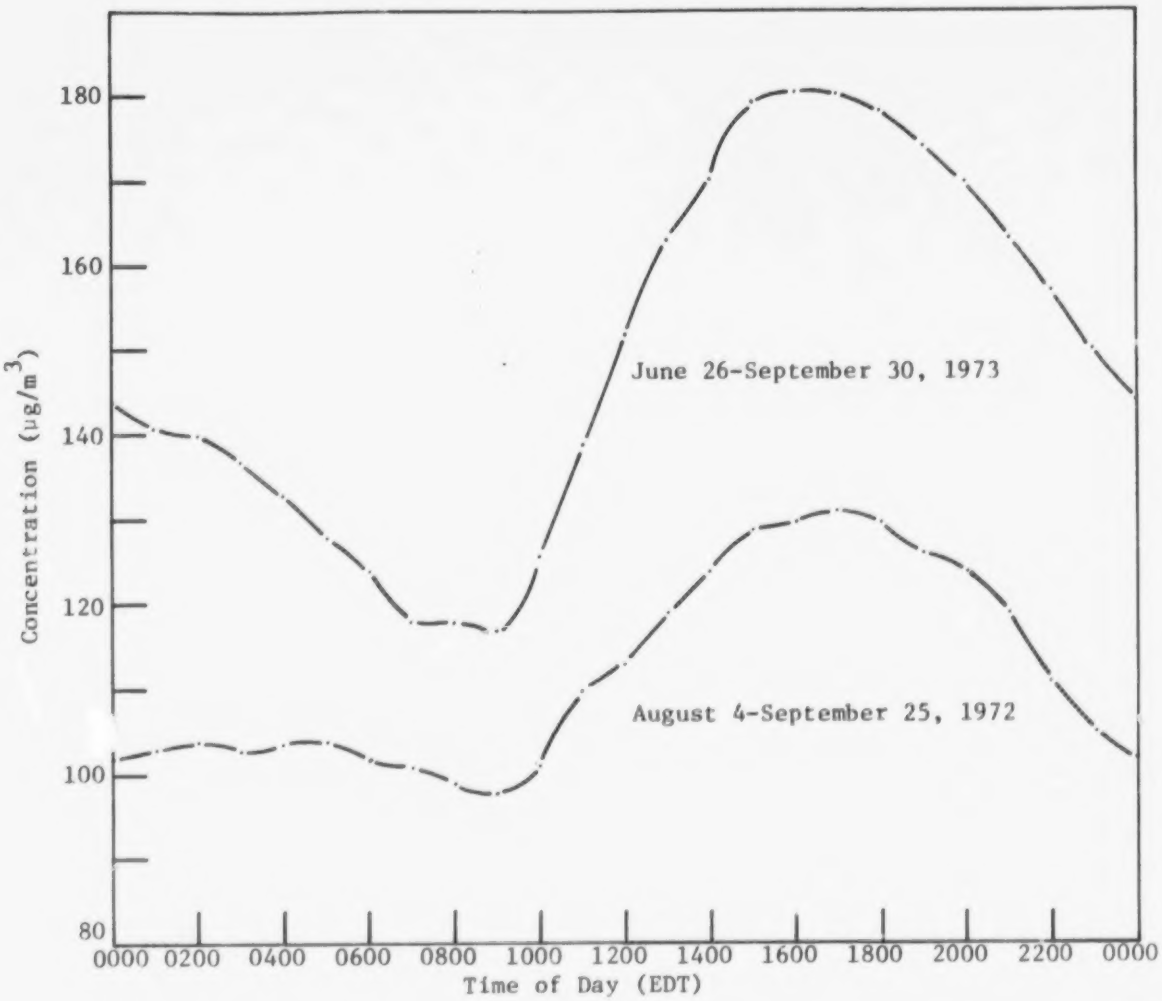
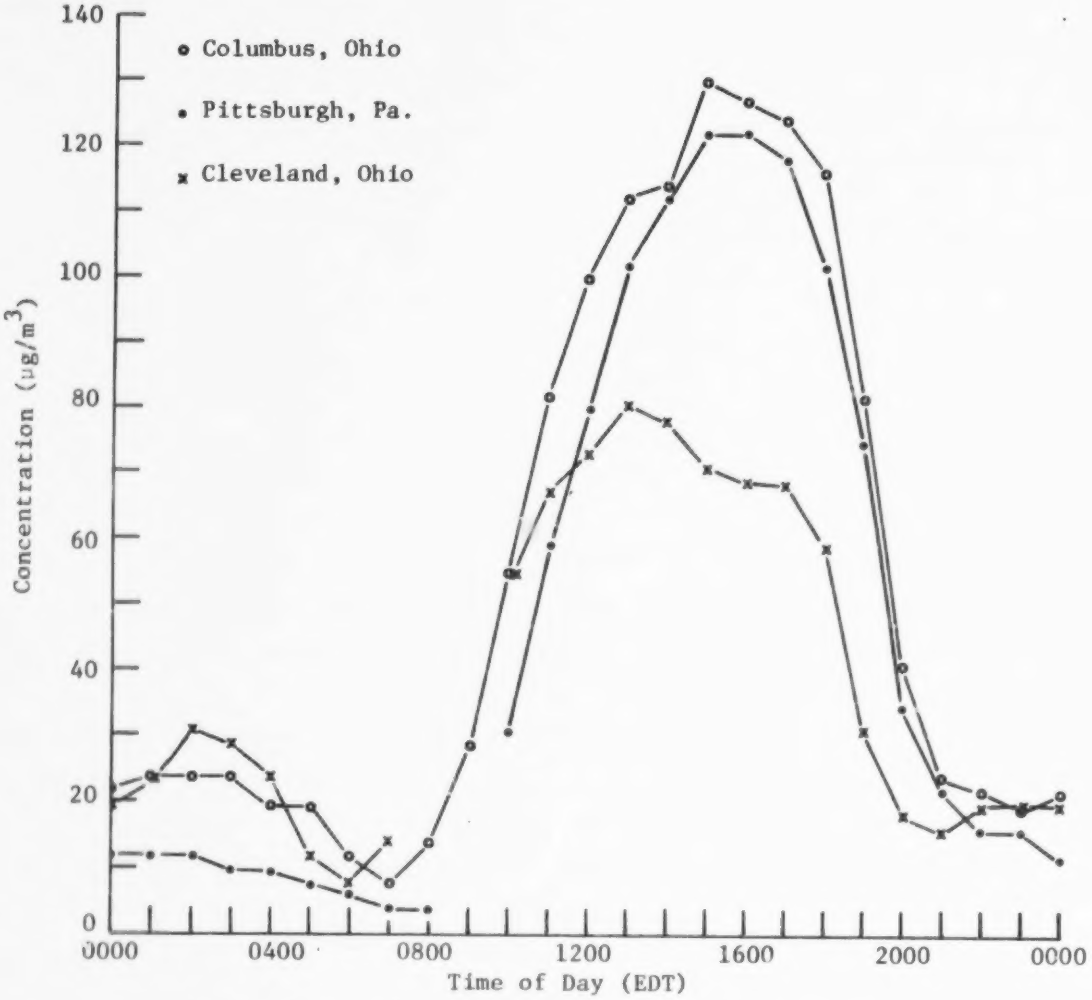


Figure 28. Mean diurnal ozone concentration at Garrett County Maryland Airport for June 26 to September 30, 1973, and August 4 to September 25, 1972.



Data Source: Ambient Ozone Measurements, July through September, 1971, Research Triangle Park, N.C.: Division of Atmospheric Surveillance, Environmental Protection Agency (1972).

Figure 29. Mean diurnal ozone concentrations at Cleveland, and Columbus, Ohio and Pittsburgh, Pennsylvania during August 1971.

Table 7. CORRELATION COEFFICIENTS FOR SIMULTANEOUS HOURLY OZONE CONCENTRATION VERSUS HOURLY NITROGEN DIOXIDE CONCENTRATION WITHIN AND BETWEEN STATIONS

	Nitrogen dioxide		
Ozone	Kane	Coshocton	Lewisburg
McHenry	0.097 (1540)[a]	0.020 (1586)	-0.133 (1491)
Kane	-0.166 (1818)	-0.192 (1922)	-0.221 (1579)
Coshocton	0.044 (1764)	-0.102 (1775)	-0.047 (1566)
Lewisburg	-0.158 (1582)	-0.050 (1627)	-0.084 (1655)

[a] Number of pairs

for simultaneous and lagged hourly ozone concentrations between station pairs are shown in Table 8.* The selection of one-, two-, and three-hour lags is based on an inspection of the mean diurnal ozone concentration curves shown in Figure 24.

Correlation coefficients and differences in coefficients significant at the .05 level for various sample sizes are shown in Table 9. Since a serial correlation approaching .9 was determined previously for hourly ozone concentration data lagged by one hour at McHenry, Maryland,[1/] Table 9 contains values for both serial correlation and no serial correlation assumptions. Since the assumption of serial correlation is consistent with the observed changes in pollutant concentration from hour to hour and provides a more conservative test of significance, the correlation coefficients reported in Tables 7 and 8 were compared with those in Table 9 that assumed serial correlation.

Thus, in Table 7, none of the coefficients is significant at the .05 level with the exception of the Kane ozone-Lewisburg nitrogen dioxide comparison which is marginally significant. Since many of the nitrogen

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*Correlation coefficients were computed using the BMDX 84 "Asymetrical Correlation with Missing Data" program.

Table 8. CROSS CORRELATION COEFFICIENTS FOR SIMULTANEOUS AND LAGGED HOURLY OZONE CONCENTRATION BETWEEN PAIRS OF STATIONS

Fixed station	Lagged station															
	McHenry				Kane				Coshocton				Lewisburg			
	Lag hours															
	0	1	2	3	0	1	2	3	0	1	2	3	0	1	2	3
McHenry					0.531 (1501)[a]	0.531 (1501)	0.517 (1501)	0.492 (1502)	0.678 (1487)	0.672 (1487)	0.649 (1487)	0.616 (1487)	0.472 (1457)	0.480 (1456)	0.464 (1454)	0.424 (1453)
Kane	0.531 (1501)	0.515 (1500)	0.487 (1499)	0.451 (1498)					0.534 (1725)	0.511 (1724)	0.468 (1723)	0.416 (1722)	0.468 (1543)	0.456 (1542)	0.422 (1541)	0.371 (1540)
Coshocton	0.678 (1487)	0.669 (1486)	0.645 (1485)	0.607 (1484)	0.534 (1725)	0.532 (1725)	0.510 (1725)	0.472 (1725)					0.500 (1532)	0.517 (1531)	0.505 (1530)	0.469 (1529)
Lewisburg	0.472 (1457)	0.442 (1456)	0.393 (1453)	0.329 (1452)	0.468 (1543)	0.451 (1544)	0.407 (1543)	0.342 (1543)	0.500 (1532)	0.452 (1532)	0.385 (1532)	0.302 (1533)				

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[a] Number of pairs.

Table 9. CORRELATION COEFFICIENTS AND DIFFERENCES SIGNIFICANT AT THE .05 LEVEL

Number of pairs	Serial correlation (.9)		No serial correlation	
	$\|r\|$	$\|r_1-r_2\|$	$\|r\|$	$\|r_1-r_2\|$
1450	.230	.326	.051	.073
1475	.228	.323	.051	.072
1500	.226	.320	.051	.072
1525	.224	.317	.050	.071
1550	.223	.315	.050	.070
1575	.221	.312	.049	.070
1600	.219	.310	.049	.069
1650	.216	.305	.048	.068
1700	.213	.301	.048	.067
1750	.210	.296	.047	.066
1800	.207	.292	.046	.065
1900	.201	.284	.045	.064

dioxide concentrations were below the minimum detectable concentration, caution should be exercised in assigning importance to any of the coefficients reported in Table 7. In contrast, all of the ozone-ozone comparisons (Table 8) are significant at the .05 level. Considering the station spacing, the correlation coefficients are surprisingly large. However, none of the zero lag correlation coefficients shown in Table 8 is significantly different from any other.

5.2 Supplementary Data (October 1-November 2, 1973)

In addition to the contractually required measurements at Kane, Pennsylvania, additional measurements were made at McHenry, Maryland; Coshocton, Ohio; and Lewisburg, West Virginia. Those measurements are also reported herein.

5.2.1 Summary Statistics

Means, standard deviations and case counts of hourly ozone concentrations, by station are shown in Table 10; the corresponding statistics for nitrogen dioxide are given in Table 11. At Kane, Pennsylvania, 163 cases produced a mean hourly nonmethane hydrocarbon concentration of 126.4 $\mu g/m^3$ with a standard deviation of 34.4. These data were obtained following modification of the hydrocarbon analyzer to remove the moisture interference and are considered valid. In addition several grab samples were collected in Tedlar bags by RTI personnel and submitted to Chemistry and Physics Laboratory, National Environmental Research Center, Research Triangle Park, North Carolina, for hydrocarbon analysis by gas chromatography. The analytical results as well as the comments of the analyst may be found in Appendix C.

Cumulative frequency distributions for hourly pollutant concentrations are presented in Table 12 and plotted in Figure 30. Maximum hourly ozone concentrations (concentrations exceeded during approximately one percent of hours) were 240 $\mu g/m^3$ at Kane, Pennsylvania; 170 $\mu g/m^3$ at Coshocton, Ohio; and 155 $\mu g/m^3$ at Lewisburg, West Virginia.

During this period, mean hourly ozone concentrations are lower at all stations than during the June 26 to September 30 period. Mean hourly nitrogen dioxide concentrations are similar during both periods. The NAAQS for photochemical oxidants was exceeded during approximately 19, 3, and <1 percent of the hours at Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia. It was not exceeded at McHenry, Maryland; however, it is noted that only 59 hours of data were obtained at that station. The NAAQS for hydrocarbons [160 $\mu g/m^3$ as a three-hour concentration (6-9 a.m.) not be exceeded more than once a year] was exceeded twice at Kane, Pennsylvania.

5.2.2 Diurnal Patterns

Mean pollutant concentrations for each hour of the day are shown in Table 13. Mean diurnal ozone, nitrogen dioxide, and nonmethane hydrocarbon concentration curves for Kane, Pennsylvania for October 1-31, 1973 are shown in Figure 31. Due to the small number of cases for each hour (maximum of 7), little significance should be attached to the nonmethane diurnal concentration curve. In Figure 32 it can be seen that

(Text continued on page 1-67)

Table 10. STATISTICAL SUMMARY OF HOURLY OZONE CONCENTRATION MEASUREMENTS BY STATION
October 1-November 2, 1973

Station	Mean hourly concentration ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Case count
McHenry, Maryland	87.0	19.4	59
Kane, Pennsylvania	111.3	52.9	729
Coshocton, Ohio	73.9	37.1	558
Lewisburg, West Virginia	81.8	34.3	739

Table 11. STATISTICAL SUMMARY OF HOURLY NITROGEN DIOXIDE CONCENTRATION MEASUREMENTS BY STATION
October 1-November 2, 1973

Station	Mean hourly concentration ($\mu g/m^3$)	Standard deviation ($\mu g/m^3$)	Case count
Kane, Pennsylvania	13.2	13.2	731
Coshocton, Ohio	23.6	12.9	559
Lewisburg, West Virginia	15.8	15.1	782

Table 12. CUMULATIVE FREQUENCY DISTRIBUTIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (October 1-November 2, 1973)

	Percent of samples greater than stated concentration									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Concentration (µg/m^3)	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
	100.0	100.0	100.0	100.0	100.0	100.0	0.0	100.0	100.0	0.0
0.	100.0	100.0	90.7	100.0	100.0	100.0	0.0	100.0	94.6	0.0
10.	100.0	98.2	49.9	100.0	99.5	91.2	0.0	99.7	53.3	0.0
20.	100.0	97.1	22.4	100.0	96.0	49.6	0.0	99.1	24.7	0.0
30.	100.0	94.9	10.3	100.0	89.1	25.9	0.0	95.1	15.9	0.0
40.	100.0	92.3	6.0	100.0	83.9	10.6	0.0	88.5	13.7	0.0
50.	98.3	87.8	2.5	100.0	73.0	5.4	0.0	79.0	4.7	0.0
60.	96.6	81.3	.3	100.0	60.2	1.6	0.0	70.0	.9	0.0
70.	79.7	73.7	0.0	100.0	45.5	.5	0.0	61.3	0.0	0.0
80.	59.3	69.0	0.0	100.0	34.4	0.0	0.0	49.4	0.0	0.0
90.	39.0	62.0	0.0	88.3	26.3	0.0	0.0	38.4	0.0	0.0
100.	20.3	55.5	0.0	67.5	21.5	0.0	0.0	29.5	0.0	0.0
110.	11.9	51.8	0.0	54.0	16.7	0.0	0.0	22.5	0.0	0.0
120.	6.8	43.2	0.0	46.6	13.3	0.0	0.0	15.6	0.0	0.0
130.	3.4	35.9	0.0	39.3	9.9	0.0	0.0	11.4	0.0	0.0
140.	1.7	29.7	0.0	33.1	7.0	0.0	0.0	5.3	0.0	0.0
150.	0.0	23.5	0.0	28.2	4.3	0.0	0.0	2.7	0.0	0.0
160.	0.0	19.2	0.0	22.7	2.9	0.0	0.0	.4	0.0	0.0
170.	0.0	13.3	0.0	16.0	1.3	0.0	0.0	.1	0.0	0.0
180.	0.0	9.7	0.0	8.6	.4	0.0	0.0	0.0	0.0	0.0
190.	0.0	7.3	0.0	1.8	.4	0.0	0.0	0.0	0.0	0.0
200.	0.0	5.3	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0
210.	0.0	4.3	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0
220.	0.0	2.7	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0
230.	0.0	2.5	0.0	.6	0.0	0.0	0.0	0.0	0.0	0.0
240.	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
250.	0.0	.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
260.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
270.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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* Nonmethane hydrocarbon data invalid.

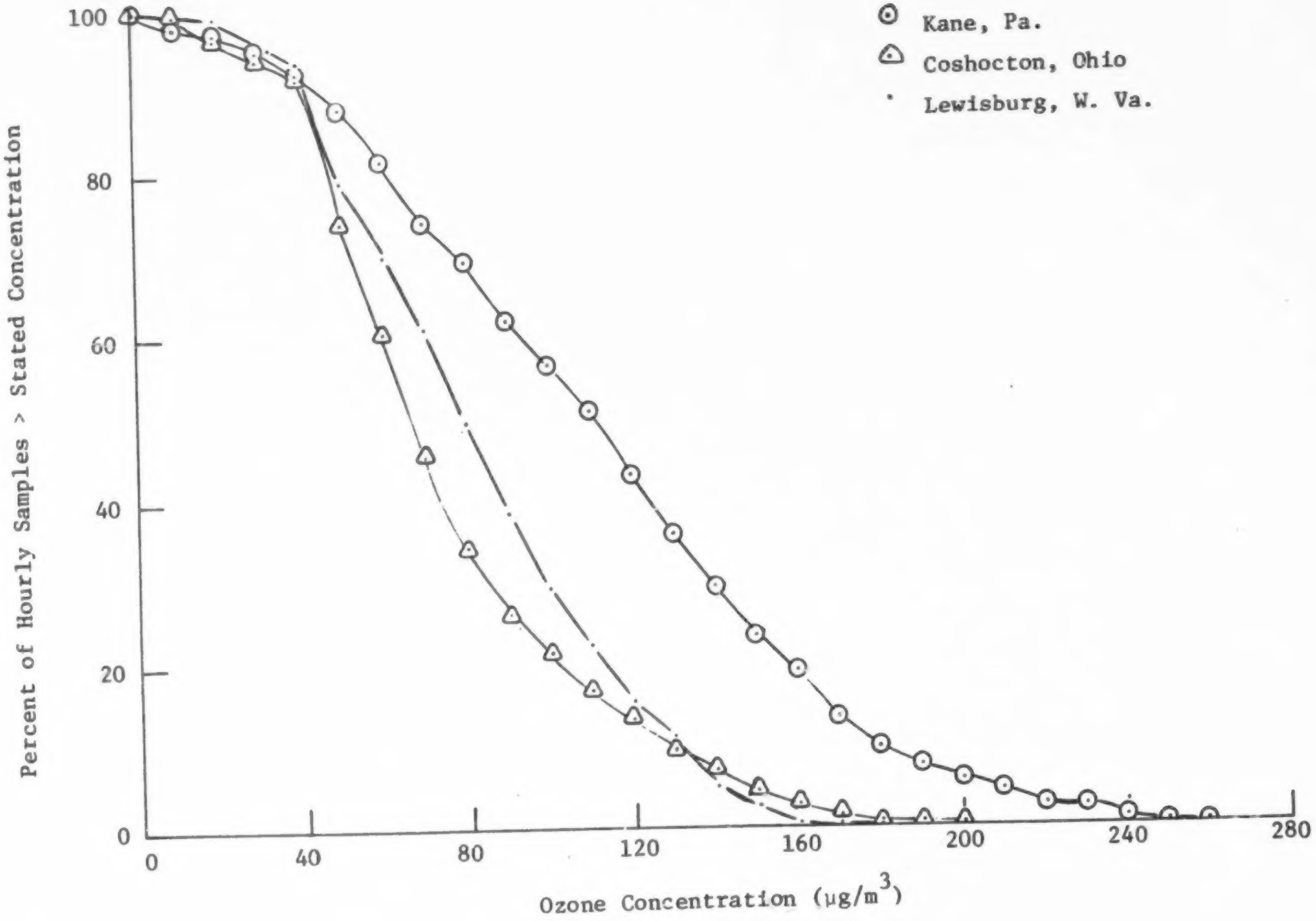

Figure 30. Frequency distribution of hourly ozone concentrations October 1 - November 2, 1973 at Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia.

Table 13. MEANS AND STANDARD DEVIATIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (October 1-November 2, 1973)

Time(EDT) at beginning of sample	Concentration ($\mu g/m^3$)										
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.			
	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
0100										
MEAN	94.7	102.4	14.3	121.9	66.0	25.8	99999.0	74.6	16.4	99999.0
STD DEV	11.9	47.0	15.8	32.0	25.7	11.7	0.0	20.7	15.7	0.0
CASES	3	31	31	7	24	24	0	32	33	0
0200										
MEAN	93.7	97.4	15.8	130.0	60.2	27.2	99999.0	69.3	14.6	99999.0
STD DEV	17.0	45.4	15.2	35.6	26.4	12.3	0.0	20.6	15.8	0.0
CASES	3	31	31	7	24	24	0	32	33	0
0300										
MEAN	90.0	97.4	14.9	137.3	55.9	27.6	99999.0	64.2	13.7	99999.0
STD DEV	23.6	42.6	13.2	47.4	25.3	13.7	0.0	19.3	15.9	0.0
CASES	3	31	31	7	24	24	0	32	33	0
0400										
MEAN	95.1	94.4	14.1	139.1	52.3	28.3	99999.0	62.3	12.7	99999.0
STD DEV	25.7	41.1	12.5	54.6	26.1	14.0	0.0	18.5	15.8	0.0
CASES	3	31	31	7	24	24	0	32	33	0
0500										
MEAN	92.9	94.3	14.4	128.3	52.0	27.5	99999.0	58.2	12.5	99999.0
STD DEV	22.7	41.7	12.7	37.9	23.2	15.0	0.0	20.3	16.0	0.0
CASES	3	31	31	7	24	24	0	32	33	0
0600										
MEAN	85.6	90.4	15.1	124.6	49.1	27.6	99999.0	55.5	12.4	99999.0
STD DEV	15.5	42.0	15.1	29.7	29.9	16.0	0.0	21.0	15.7	0.0
CASES	3	31	31	7	24	24	0	32	33	0
0700										
MEAN	83.0	88.6	15.6	123.5	44.0	29.1	99999.0	51.2	14.1	99999.0
STD DEV	6.1	40.6	14.8	29.4	24.5	19.0	0.0	18.8	16.1	0.0
CASES	3	31	31	7	24	24	0	32	33	0
0800										
MEAN	90.5	89.8	15.8	130.4	38.4	29.0	99999.0	46.9	15.6	99999.0
STD DEV	2.2	40.4	13.3	34.0	21.1	19.4	0.0	20.3	15.4	0.0
CASES	3	31	31	7	24	24	0	32	33	0

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* The 0.0 entry under Nonmethane hydrocarbon indicates invalid data; the case counts are included for information purposes.

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Table 13 (cont'd). MEANS AND STANDARD DEVIATIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (October 1-November 2, 1973)

	Concentration ($\mu g/m^3$)									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
Time(EDT) at beginning of sample	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
0900										
MEAN	74.1	89.0	17.4	138.3	39.9	26.8	99999.0	44.4	17.6	99999.0
STD DEV	1.7	39.3	12.6	29.2	16.0	15.9	0.0	29.0	15.9	0.0
CASES	3	31	31	6	23	24	0	32	33	0
1000										
MEAN	76.5	92.6	16.9	157.2	46.7	27.9	99999.0	52.9	16.7	99999.0
STD DEV	11.3	37.7	14.7	31.5	12.3	12.5	0.0	29.0	16.1	0.0
CASES	3	30	30	6	22	23	0	31	33	0
1100										
MEAN	74.8	101.4	14.9	134.5	49.4	27.3	99999.0	70.3	16.9	99999.0
STD DEV	29.5	44.5	13.4	27.6	15.2	11.6	0.0	24.9	17.0	0.0
CASES	2	30	30	6	24	23	0	31	33	0
1200										
MEAN	95.6	109.5	13.8	125.7	62.7	25.1	99999.0	90.7	15.2	99999.0
STD DEV	40.4	49.0	13.9	28.9	15.9	11.6	0.0	26.2	14.0	0.0
CASES	2	30	30	6	23	22	0	32	32	0
1300										
MEAN	101.7	119.1	10.7	107.5	76.7	25.2	99999.0	104.7	13.9	99999.0
STD DEV	49.1	53.5	11.8	24.1	21.9	12.1	0.0	28.5	12.7	0.0
CASES	2	30	31	6	23	22	0	31	33	0
1400										
MEAN	99.3	127.2	9.7	119.1	91.1	22.5	99999.0	114.2	13.0	99999.0
STD DEV	36.9	56.0	11.5	38.5	25.4	9.6	0.0	29.0	12.2	0.0
CASES	3	31	31	7	23	23	0	31	33	0
1500										
MEAN	98.7	133.8	6.5	121.8	101.0	20.9	99999.0	110.4	13.3	99999.0
STD DEV	4.9	59.9	11.2	45.1	29.3	8.8	0.0	29.5	12.9	0.0
CASES	2	31	30	7	23	23	0	30	33	0
1600										
MEAN	92.6	147.3	7.5	117.9	107.7	19.7	99999.0	120.2	13.1	99999.0
STD DEV	5.8	61.2	10.4	34.8	33.1	8.9	0.0	30.3	13.3	0.0
CASES	2	30	30	7	23	23	0	30	32	0

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* The 0.0 entry under Nonmethane hydrocarbon indicates invalid data; the case counts are included for information purposes.

Table 13 (cont'd). MEANS AND STANDARD DEVIATIONS OF HOURLY CONCENTRATIONS OF OZONE, NITROGEN DIOXIDE, AND NONMETHANE HYDROCARBON BY STATION (October 1-November 2, 1973)

Time(EDT) at beginning of sample	Concentration ($\mu g/m^3$)									
	McHenry, Md.	Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
	Ozone	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*	Ozone	Nitrogen dioxide	Nonmethane hydrocarbon*
1700										
MEAN	83.7	145.4	7.5	117.9	111.0	18.6	99999.0	115.3	13.6	99999.0
STD DEV	18.7	64.7	12.3	33.1	30.7	10.9	0.0	32.4	13.6	0.0
CASES	2	30	30	7	23	23	0	24	32	0
1800										
MEAN	95.6	142.5	9.6	120.4	112.4	16.4	99999.0	114.4	16.5	99999.0
STD DEV	23.9	63.8	11.7	34.7	33.4	8.5	0.0	28.4	14.0	0.0
CASES	2	30	30	7	23	23	0	30	32	0
1900										
MEAN	70.1	137.3	12.7	123.2	109.2	15.6	99999.0	111.7	20.0	99999.0
STD DEV	27.7	57.1	11.7	29.9	32.9	6.1	0.0	24.4	13.3	0.0
CASES	2	30	30	7	23	23	0	27	32	0
2000										
MEAN	71.5	125.9	14.6	125.4	106.0	17.1	99999.0	103.3	20.0	99999.0
STD DEV	33.9	55.3	12.4	35.9	33.9	7.7	0.0	25.5	16.1	0.0
CASES	2	30	30	7	23	23	0	30	32	0
2100										
MEAN	78.7	122.4	12.7	123.5	98.4	17.3	99999.0	96.2	20.1	99999.0
STD DEV	33.6	55.5	12.7	36.1	33.9	9.1	0.0	25.1	15.8	0.0
CASES	2	30	30	7	23	23	0	31	32	0
2200										
MEAN	62.7	116.1	12.8	126.3	91.8	19.3	99999.0	86.6	21.5	99999.0
STD DEV	29.3	57.0	13.0	39.8	32.2	8.3	0.0	25.9	15.4	0.0
CASES	2	29	30	7	23	23	0	31	32	0
2300										
MEAN	64.1	109.5	14.3	124.9	85.6	18.2	99999.0	83.1	19.0	99999.0
STD DEV	22.5	57.5	13.5	37.2	27.7	7.2	0.0	22.9	15.5	0.0
CASES	2	29	30	7	23	23	0	31	32	0
2400										
MEAN	87.3	107.5	13.9	119.4	77.3	20.7	99999.0	76.7	17.1	99999.0
STD DEV	8.7	49.3	14.2	31.4	24.3	9.7	0.0	21.5	15.3	0.0
CASES	2	30	30	7	23	23	0	31	32	0

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* The 0.0 entry under Nonmethane hydrocarbon indicates invalid data; the case counts are included for information purposes.

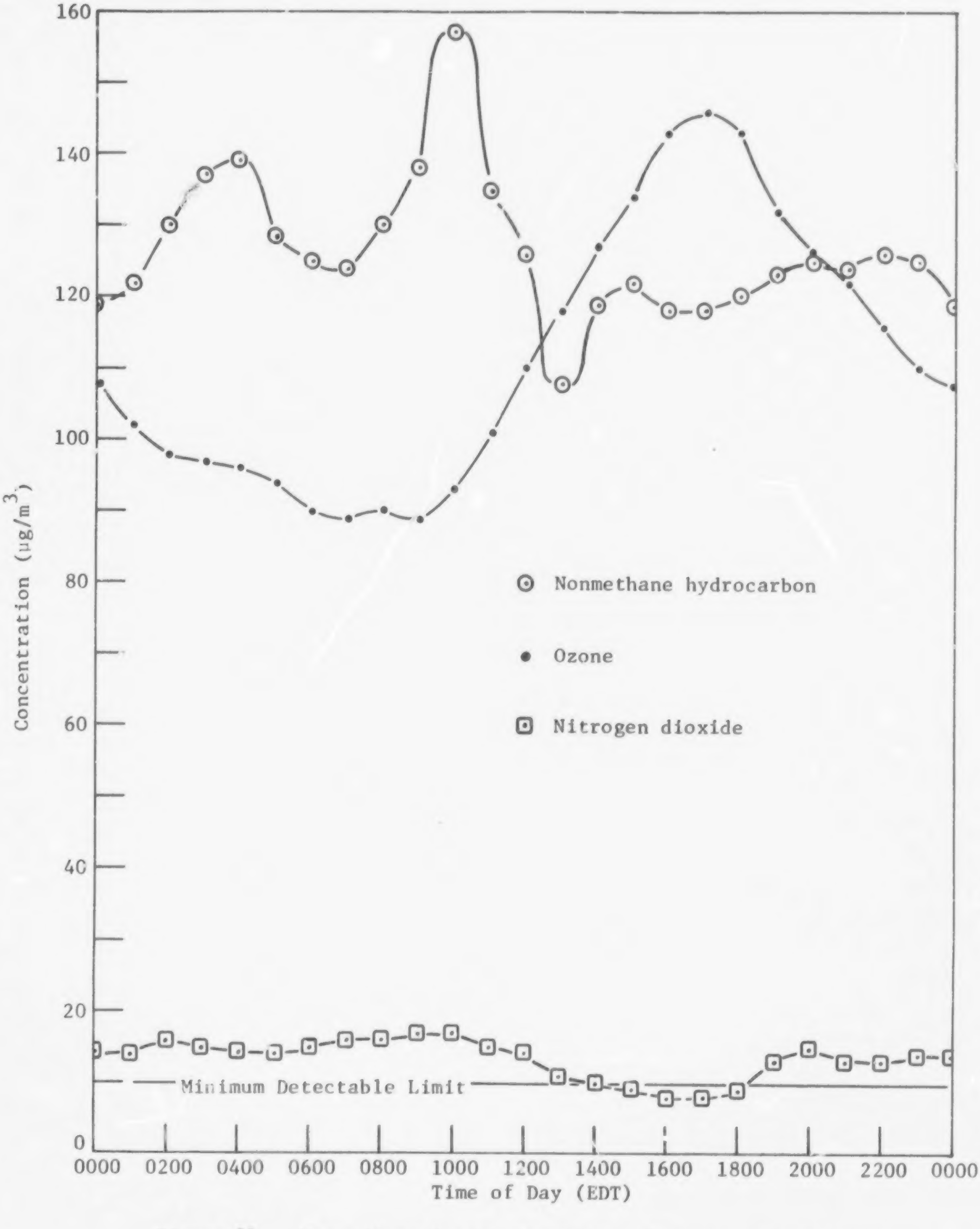

Figure 31. Mean diurnal concentrations of ozone and nitrogen dioxide from October 1-31 and nonmethane hydrocarbon from October 16-31, 1973 at Kane, Pennsylvania.

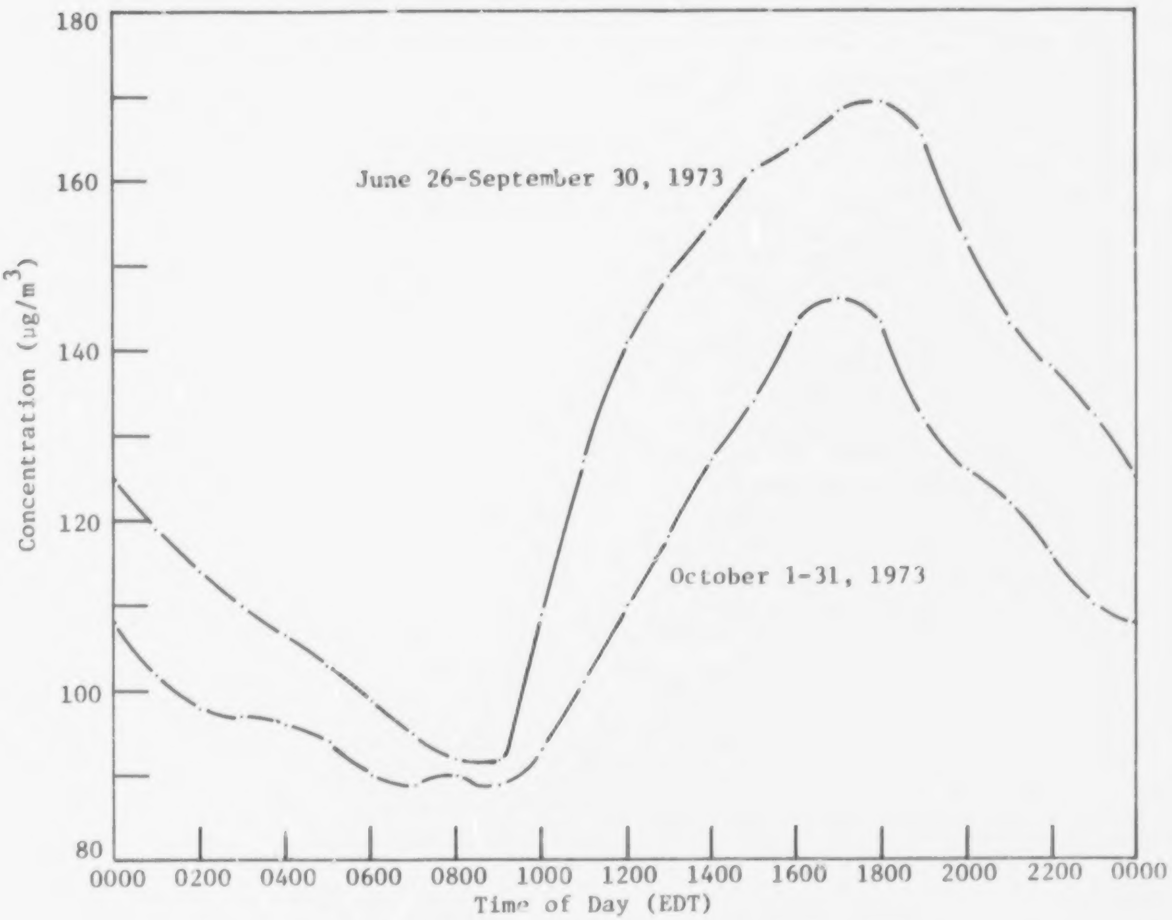

Figure 32. Mean diurnal ozone concentrations at Kane, Pennsylvania for June 26 to September 30 and October 1 to 31, 1973.

mean ozone concentrations at Kane, Pennsylvania during October 1973 are lower at all hours of the day than during the June 26-September 1973 period.

Mean diurnal curves of ozone and nitrogen dioxide concentrations at Kane, Pennsylvania, Coshocton, Ohio; and Lewisburg, West Virginia are shown in Figures 33 and 34, respectively.

5.2.3 Effect of Change of Season

The primary reason for extending the monitoring period at Kane, Pennsylvania was to examine the effect of change of season, in particular the onset of freezing temperatures, on ozone concentrations.

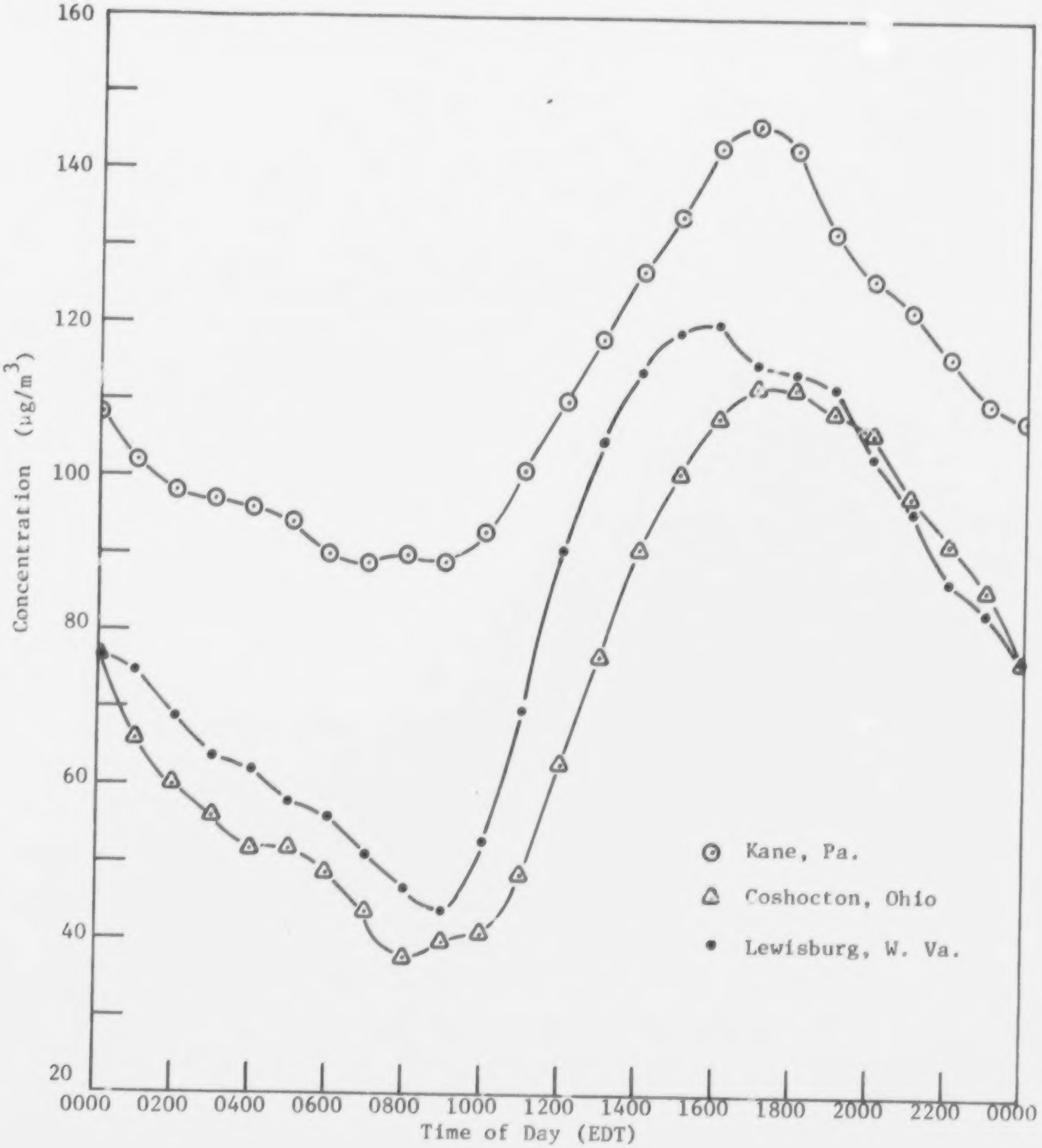

Figure 33. Mean diurnal ozone concentrations at Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia from October 1 to November 2, 1973.

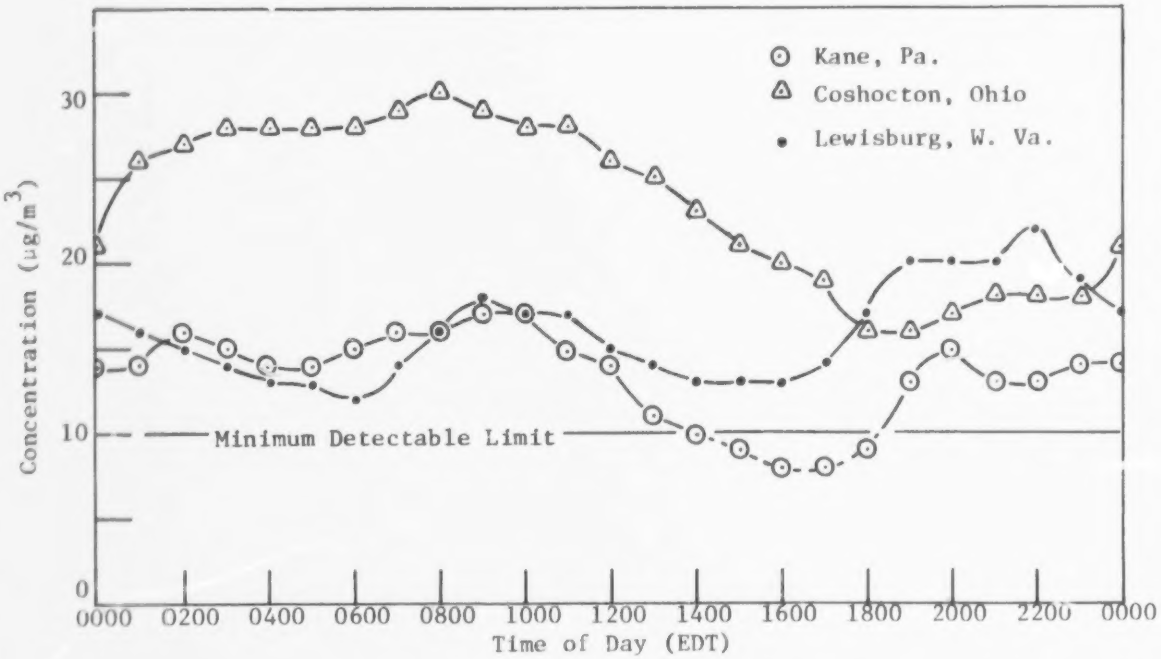

Figure 34. Mean diurnal nitrogen dioxide concentrations at Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia from October 1 to November 2, 1973.

It is known that hydrocarbon species capable of participating in the photochemical generation of ozone are emitted by trees and other forms of vegetation. It was speculated therefore, that with the death of leaves due to frost, the emission of hydrocarbon species from trees would decrease and further that such a decrease might lead to reduced ozone concentrations. In Figure 35 mean daily ozone concentrations and minimum daily temperatures for September and October 1973 are compared. Freezing temperatures occurred on September 19 and 21 (the usual date for the first killing frost is September 23) and again in October, yet higher mean daily ozone concentrations occurred during October. Obviously, no simple relationship between freezing temperatures and ozone concentrations exists.

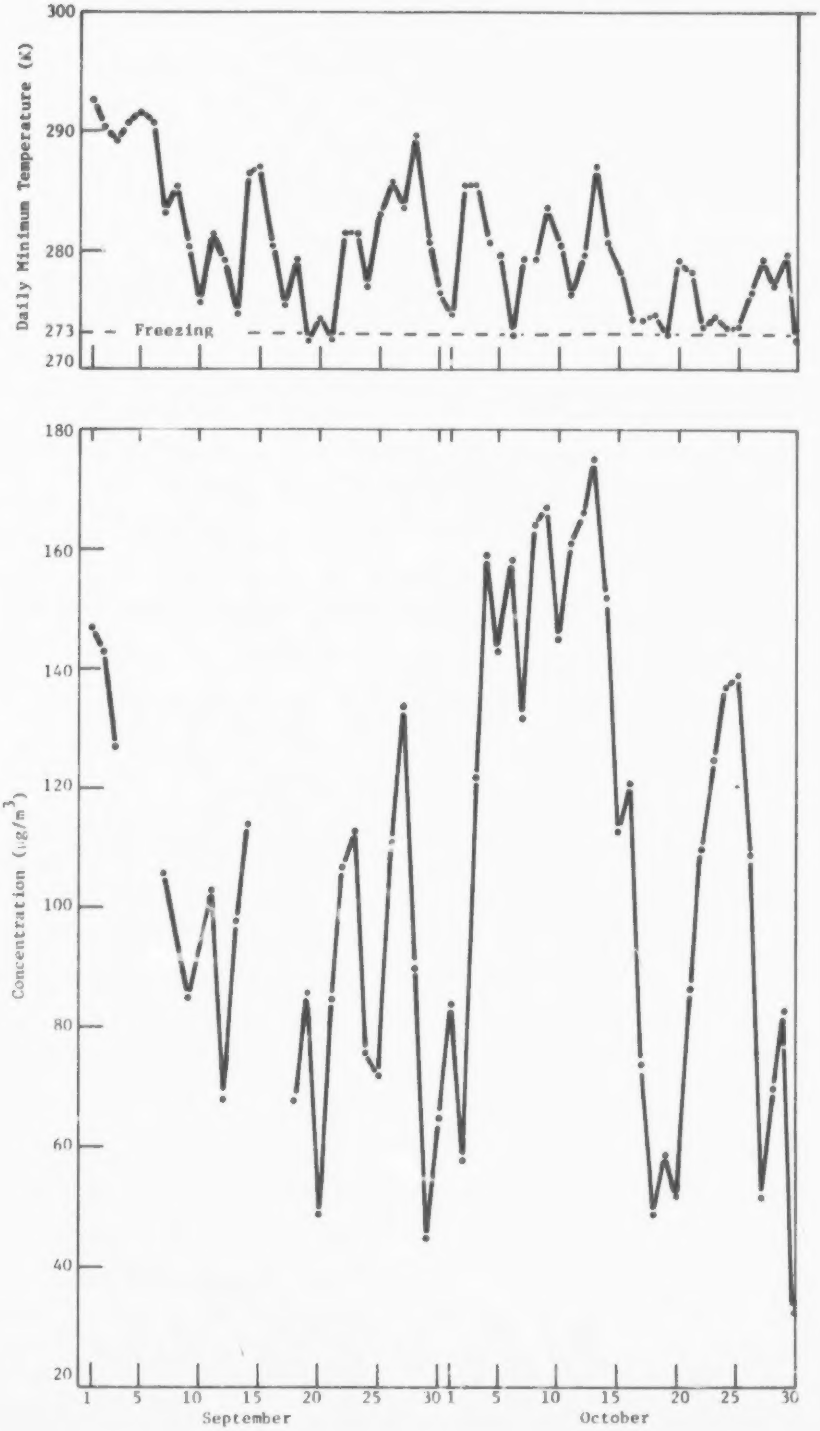

Figure 35. Mean daily ozone concentration at Kane, Pennsylvania and daily minimum temperature at Bradford (Pennsylvania) Regional Airport for September and October 1973.

6.0 CONCLUSIONS

The principal conclusions arising from the statistical examination of the data collected during the summer of 1973 are as follows:

1) The NAAQS for photochemical oxidants (160 $\mu g/m^3$ for one hour not to be exceeded more than once per year) was exceeded during approximately 37, 30, 20, and 15 percent of the hours at McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia, respectively from June 26 to September 30, 1973.

2) Nitrogen dioxide concentrations were at or near background levels at Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia.

3) Mean diurnal ozone concentration curves for the four stations are very similar, varying mainly in magnitude of hourly ozone concentration.

4) High correlations (.468-.678) significant at the .05 level exist between simultaneous hourly ozone concentrations measured at the four stations. The differences in the ozone-ozone correlation coefficients are not significant.

5) There is no apparent lag effect, i.e., changes in ozone concentration at one station do not lag behind changes in ozone concentration at the other stations for the lags investigated.

6) The occurrence of high ozone concentrations at nonurban locations is widespread, affecting a four-state area in eastern United States.

REFERENCES

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2. Mount Storm, West Virginia-Gorman, Maryland, and Luke, Maryland-Keyser, West Virginia, Air Pollution Abatement Activity. Air Pollution Control Office Publ. No. APTD-0656. Research Triangle Park, N.C.: Environmental Protection Agency, April 1971.

3. Richter, H. G. Special Ozone and Oxidant Measurements in Vicinity of Mount Storm, West Virginia. Research Triangle Park, N.C.: Research Triangle Institute, October 1970.

4. Ripperton, L. A., H. Jeffries, and J. J. B. Worth. Natural Synthesis of Ozone in the Troposphere. Environ. Sci. and Tech. 5, 246-248, 1971.

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6. Wunderle, J. Personal communication to W. D. Bach, Jr., 1973.

7. Beard, C. Personal communication to J. J. B. Worth, 1973.

8. Hodgeson, J. A., R. K. Stevens, and B. E. Martin. A Stable Ozone Source Applicable as a Secondary Standard for Calibration of Atmospheric Monitors. Air Quality Instrumentation, Vol. 1, John Scales, ed., 149-150, ISA, Pittsburgh, Pa, 1972.

APPENDIX A

CALIBRATION METHODS AND PROCEDURES

Dynamic calibration procedures were used to calibrate all analyzers used during the field measurement period. Biweekly calibrations were performed on each instrument using the procedures described below.

A-1 General

Because the four stations were at elevations above mean sea level adjustments to the data were necessary to reduce values to reference condition of 25°C (298K) and 760 mm Hg. Adjustments to volume measurements were made using the following equation:

$$V_R = V \times \frac{P}{760} \times \frac{298}{t + 273}$$

where

V_R = volume of air at reference conditions, liters,
V = volume of air at sampling conditions, liters,
P = barometric pressure at sampling conditions, mm Hg, and
t = temperature at sampling conditions, °C.

Table A-1 summarizes the sampling conditions assumed for each site.

Table A-1. ALTITUDE-PRESSURE RELATIONSHIP FOR SAMPLING SITES

Station	Altitude above mean sea level		Room temperature, °C	Barometric pressure mm Hg[a]	Volume of 1 liter at reference conditions (25°C, 760 mm Hg)-liters
	meters	feet			
McHenry, Md.	885	2,900	25 ± 2°	682.5	0.90
Lewisburg, W.Va.	705	2,301	25 ± 2°	697.7	0.92
Kane, Pa.	630	2,060	25 ± 3°	704.1	0.93
Coshocton, Ohio	354	1,160	25 ± 3°	727.7	0.96

[a] Derived from Table p. 9-4, Handbook of Air Pollution, PHS Publication No. 999-AP-44. "Barometric Pressure at Various Altitudes."

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The same adjusted volume was used each time a calibration was performed.

The general procedure followed during a typical calibration of any analyzer was as follows:

1) The portable calibration unit (described below) and Spectronic 20 spectrophotometer were turned on and allowed to warm up for 30 minutes. During this time, the potassium iodide (KI) sampling train was assembled and the volume flow rates of analyzers, the sampling train, and the calibration unit were checked and adjusted as necessary with a wet test meter and/or a bubble flowmeter.
2) The analyzer sample inlet line (or calibration gas inlet line in the case of the hydrocarbon analyzer) was disconnected from ambient air and connected to a source of zero air. The time of each operation was noted both in the instrument logbook and on the strip chart recorder. The instrument was allowed to sample zero air for a period of time sufficient to establish a valid zero output. This was best discerned by observing and noting the digital voltmeter output and the strip chart recorder trace. Then a known concentration of calibration gas was introduced (~80% of full-scale response) and the readings recorded after the signal stabilized. No adjustments were made to any part of the analyzer system prior to completing this step.
3) If the need for adjustment was indicated by zero and/or span drift or maintenance was required; it was done; then a dynamic multiple point calibration of the system was performed by introducing successive pollutant concentrations approximating 10, 20, 40, 60, and 80 percent of the operating range of the instrument. From the record of the instrument output, a calibration curve was constructed for use in data reduction. Steps (2) and (3) constituted the preliminary and final calibrations, respectively.
4) The analyzers were again connected to ambient air.

A-2 Ozone Analyzers

A dynamic calibration system producing ozone by ultraviolet irradiation of oxygen[A-1] was used to calibrate the gas-phase chemiluminescent ozone analyzers. The ozone generator consisted of a shielded mercury vapor lamp (20.3-cm in length) which irradiated clean compressed air flowing through a quartz tube (1.5-cm in diameter). By varying the length of the lamp exposed to the air and the total flow of compressed air (usually set at 5.0 l/min), ozone concentrations from zero to approximately 1 ppm (1960 $\mu g/m^3$) were produced.

A portable calibration unit consisting of a regulated power supply, zero air source, calibrated rotameter, ozone generator, mass flowmeter for nitric oxide mixtures, and a glass manifold with sampling ports was assembled. This unit was transported from site to site for calibration of each ozone (as well as nitrogen dioxide) analyzer. A schematic diagram of the ozone calibration system is shown in Figure A-1.

In order to obtain a reference measure of the ozone output of the calibration unit, the neutral-buffered KI analysis method[A-2] was used for each calibration point. Figure A-1 shows the arrangement of the two impingers containing the absorbing reagent. The analyzer and the bubbler train sampled simultaneously from the glass manifold. The volumetric flow (~1.0 l/min) through the KI sampling train was determined with a calibrated wet test meter as shown in Figure A-2.

The stepwise calibration procedure was as follows:

1) Install the ozone generator, allowing it to warm up for 30 minutes. Check and set all volume flowrates with a wet test meter. Set up KI sampling train and adjust sampling rate to 1 l/min.
2) Flush the system with a large concentration of ozone by adjusting the sleeve to uncover the UV lamp 15 cm. After several minutes, close the sleeve entirely and flush with zero air.

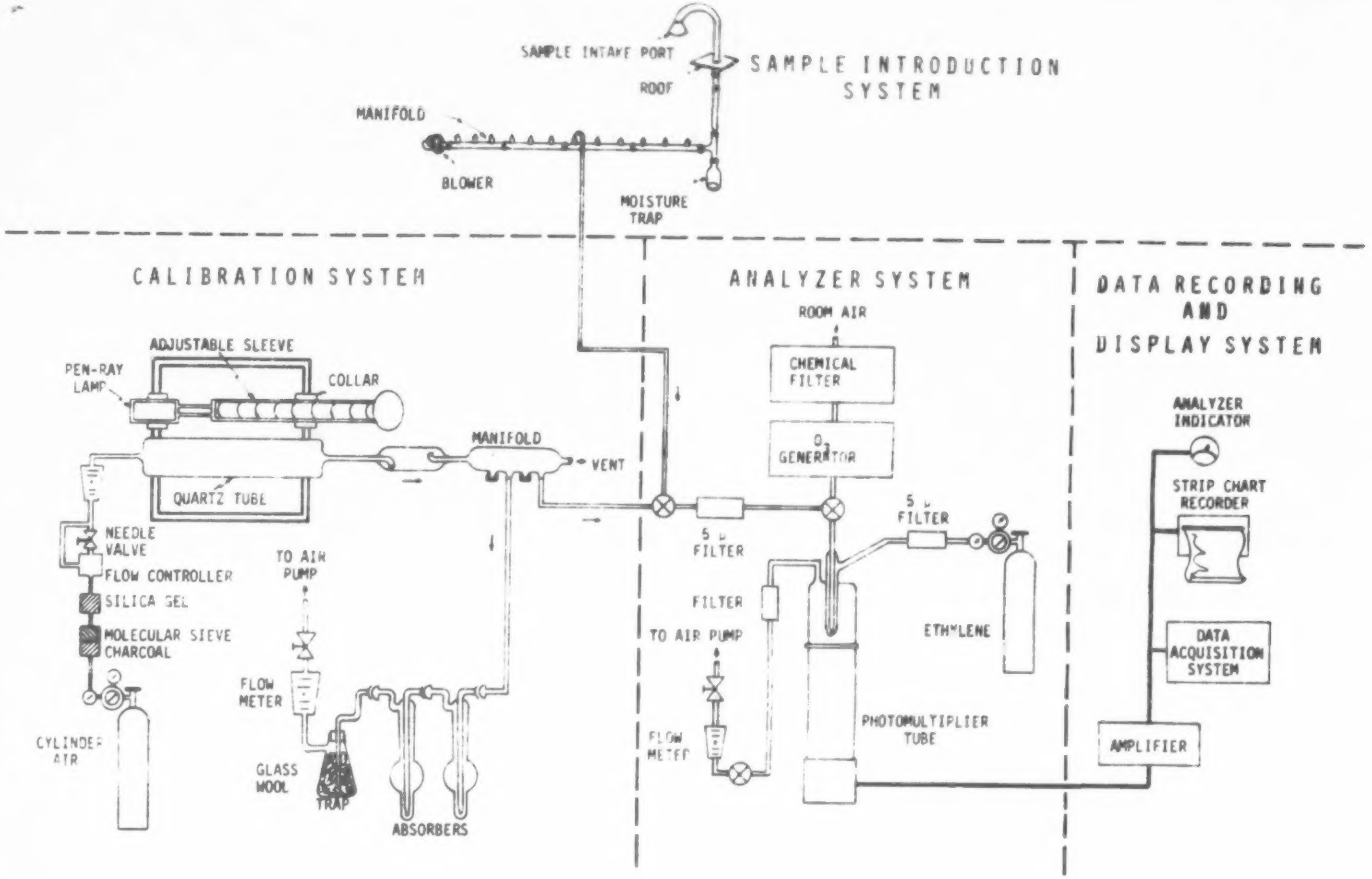
SAMPLE INTAKE PORT
ROOF
SAMPLE INTRODUCTION SYSTEM
MANIFOLD
BLOWER
MOISTURE TRAP
CALIBRATION SYSTEM
ANALYZER SYSTEM
DATA RECORDING AND DISPLAY SYSTEM
ADJUSTABLE SLEEVE
PEN-RAY LAMP
COLLAR
MANIFOLD
VENT
QUARTZ TUBE
NEEDLE VALVE
FLOW CONTROLLER
SILICA GEL
MOLECULAR SIEVE CHARCOAL
CYLINDER AIR
TO AIR PUMP
FLOW METER
GLASS WOOL
TRAP
ABSORBERS
ROOM AIR
CHEMICAL FILTER
O_3 GENERATOR
5 µ FILTER
5 µ FILTER
FILTER
TO AIR PUMP
FLOW METER
ETHYLENE
PHOTOMULTIPLIER TUBE
ANALYZER INDICATOR
STRIP CHART RECORDER
DATA ACQUISITION SYSTEM
AMPLIFIER

Figure A-1. Ozone calibration system flow chart.

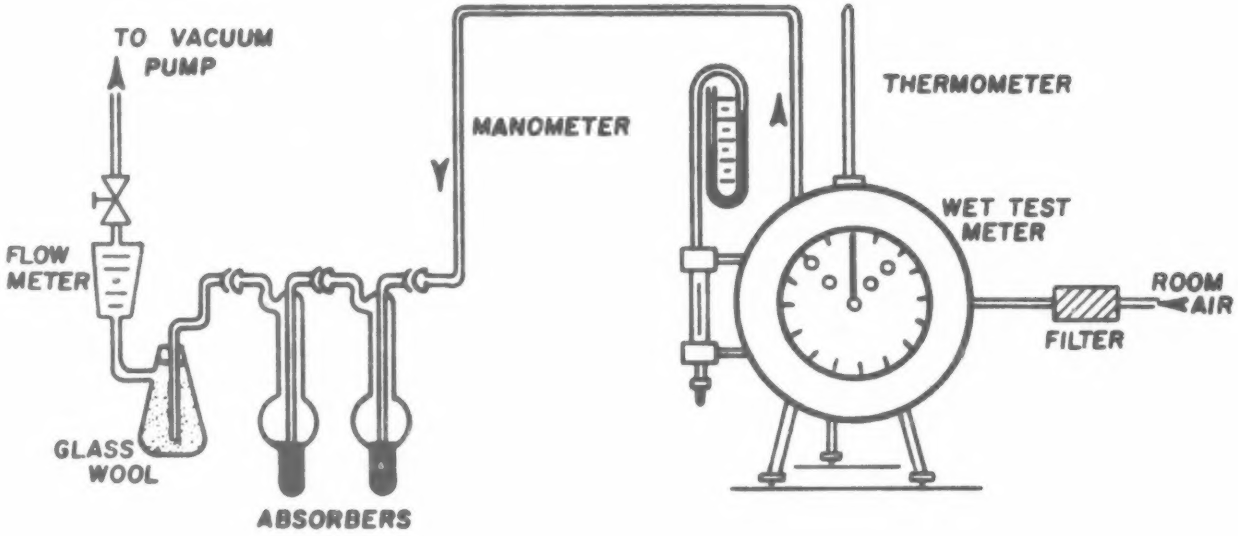
TO VACUUM PUMP
FLOW METER
GLASS WOOL
ABSORBERS
MANOMETER
THERMOMETER
WET TEST METER
FILTER
ROOM AIR

Figure A-2. Apparatus for calibration of KI sampling train flow rate under operational conditions.

3) Connect the ambient sampling line from the analyzer to the calibration manifold. After 10 minutes, record the zero point in mv output and chart divisions.

4) Pull the sleeve to uncover 1.50cm of the UV lamp. Allow the output to stabilize for 10 minutes and then connect KI bubbler train. Sample long enough to produce a detectable color change in the neutral buffered KI solution.

5) Establish the slope of the spectrophotometer calibration curve. With a 2.54cm cuvette, the spectrophotometer employed in this study gave a slope equivalent to 1.02 μg O_3/ml absorbing reagent/absorbance unit (a.u.). The same cuvette was used for the entire study. The spectrophotometer was calibrated with standard iodine solution[A-2] on two occasions: at the beginning of the study and midway through the study.

6) Measure the absorbance of the KI solution at 352nm using the spectrophotometer. Repeat the KI bubbler procedure and obtain a second absorbance value at the same sleeve setting. If the agreement is reasonable (± 5%) for identical sampling conditions, proceed to larger sleeve settings and repeat the procedure.

7) Compute the concentration of ozone in μg/m^3 for each sleeve setting as follows:

   a) Determine the volume of air sampled by the KI bubbler assembly and correct it to reference conditions of 25°C and 760mm Hg as follows:

$$V_R = V \times \frac{P}{760} \times \frac{298}{t + 273} \times 10^{-3}$$

V_R = volume of air at reference conditions, m^3,

V = volume of air at sampling conditions, liters,

P = barometric pressure at sampling conditions, mm HG,

t = temperature at sampling conditions, °C, and

10^{-3} = factor converting liters to m^3.

   b) Solve for μg/m^3 as follows:

$$O_3, \mu g/m^3 = \frac{(\text{absorbance})(1.02\ \mu g\ O_3/\text{ml/a.u.})(10\ \text{ml KI reagent})}{V_R}$$

For example:

Station: Kane, Pennsylvania
Sleeve setting: 2 cm
Volume sampled under site conditions: 10 l
Pressure: 704.1 mm Hg
Temperature: 25°C
KI absorbance: 0.105

$$O_3, \mu g/m^3 = \frac{(0.105 \text{ a.u.})(1.02 \ \mu gO_3/\text{ml/a.u.})(10 \text{ ml})}{0.0093 \text{ m}^3} = 115.2 \ \mu g/m^3$$

8) From the instrument output in mV and the ozone concentrations, prepare a calibration curve for the analyzer.

A-3 Nitrogen Dioxide Analyzer

The NO-NO_2-NO_x analyzer was calibrated by gas-phase titration.A-3/ The technique makes use of the rapid gas phase reaction between NO and O_3 to produce a stoichiometric quantity of NO_2.

After the preliminary zero and span checks, the first step in the final calibration is the introduction of zero air into the analyzer. After 10 minutes, a zero reading is taken on the NO, NO_2, and NO_x channels.

Before transporting the NO calibration gas cylinders to the field, the NO concentration of the contained calibration gases was verified using the technique of Hodgeson and associates.A-3/ The procedure consisted of titrating an NO concentration of 1.0 ppm with successive concentrations of ozone (0-0.8 ppm) produced by an ozone generator referenced to the neutral-buffered KI procedure. The resultant NO detector outputs, after stabilization at each titration points (i.e., 0.0, 0.1, 0.2, ... 0.8 ppm ozone added), were plotted as concentrations ppm (y-axis) versus O_3 concentration added, ppm (x-axis). A straight line drawn through the linear portion of the titration curve was extrapolated to the x-axis. The concentration at the x-axis intercept, C_0', was the O_3 concentration equivalent to the initial diluted NO concentration. The cylinder NO concentration was then calculated as follows:

$$C_{NO} = \frac{F_O \times C'_O}{F_{NO}}$$

where

C_{NO} = cylinder NO concentration, ppm,
F_{NO} = measured NO flow, ml/min,
C'_O = equivalence point O_3, concentration, ppm, and
F_O = total clean air flow, ml/min.

The NO portion of the analyzer was calibrated by dynamic flow dilution of the cylinder gas. This was accomplished by metering the NO from the cylinder through a calibrated mass flowmeter and then into the dilution system of the ozone generator. To calibrate the NO_2 portion of the analyzer, a constant NO concentration of approximately 940 $\mu g/m^3$ (0.5 ppm) was produced by dilution. Ozone was added in increments from the generator. Decrements observed on the spanned NO detector, are then equivalent to the NO_2 concentration produced by the O_3 source. Since the NO_2 produced was equivalent to O_3 consumed, the calibrated O_3 source served as a calibrated NO_2 source when NO was present in excess. After adequate time (~10 min) for stabilization at each point, the mV output of each channel was recorded.

The NO_2 concentration was deduced from the decrease of the NO signal, and a calibration curve relating NO_2 concentration and analyzer mV output was constructed.

A-4 Hydrocarbon Analyzer

Nonmethane hydrocarbons were determined at three stations using the Bendix Model 8201 Ambient Hydrocarbon Analyzer. Calibration was accomplished using hydrocarbon-free air as zero gas and mixtures of methane in hydrocarbon-free air as span gases. The calibration gases were purchased from Scott Research Laboratories who certified the contents of each gas bottle.

By appropriate valve switching, it was possible to use the methane to calibrate the total hydrocarbon (THC), methane, and nonmethane hydrocarbon (NMHC) channels. The zero and span calibration steps were as follows:

ZERO

1) Place sample valve (#1) and backflush valve (#2) on off position and meter/output switch in electrometer position.
2) Observe recorder baseline while component gates are open (i.e., CH_4 light on and THC light on).
3) Adjust zero control for the THC and CH_4 to zero by observing recorder output ot meter while switched to appropriate output.
4) After one complete cycle, adjust nonmethane zero control for zero indication on recorder or meter.
5) Return valves #1 and #2 to auto position.
6) Connect zero air cylinder for dynamic zero; flow rate of 200 ml/min. Switch operating mode switch to calibrate.
7) Compare mV readings with previous zero data and record; discrepancies suggest contamination.

SPAN

1) Connect cylinder containing highest concentration to the calibration inlet. Set flow rate at 200 ml/min.
2) After at least two cycles, set the span control for THC and CH_4 to the appropriate mV reading.
3) After completing the span operation on THC and CH_4, switch output to electrometer position.
4) Observe strip chart for one cycle. Manually override valve #1 to the off position for the duration shown on the strip chart in Figure A-3. This will cause the CH_4 output to equal the THC output.
5) Adjust the nonmethane span control to give the appropriate mV reading with the output switched to nonmethane.
6) Run additional calibration cylinders and record mV readings, but do not adjust span controls.
7) Recheck nonmethane calibration as outlined above for each calibration level.

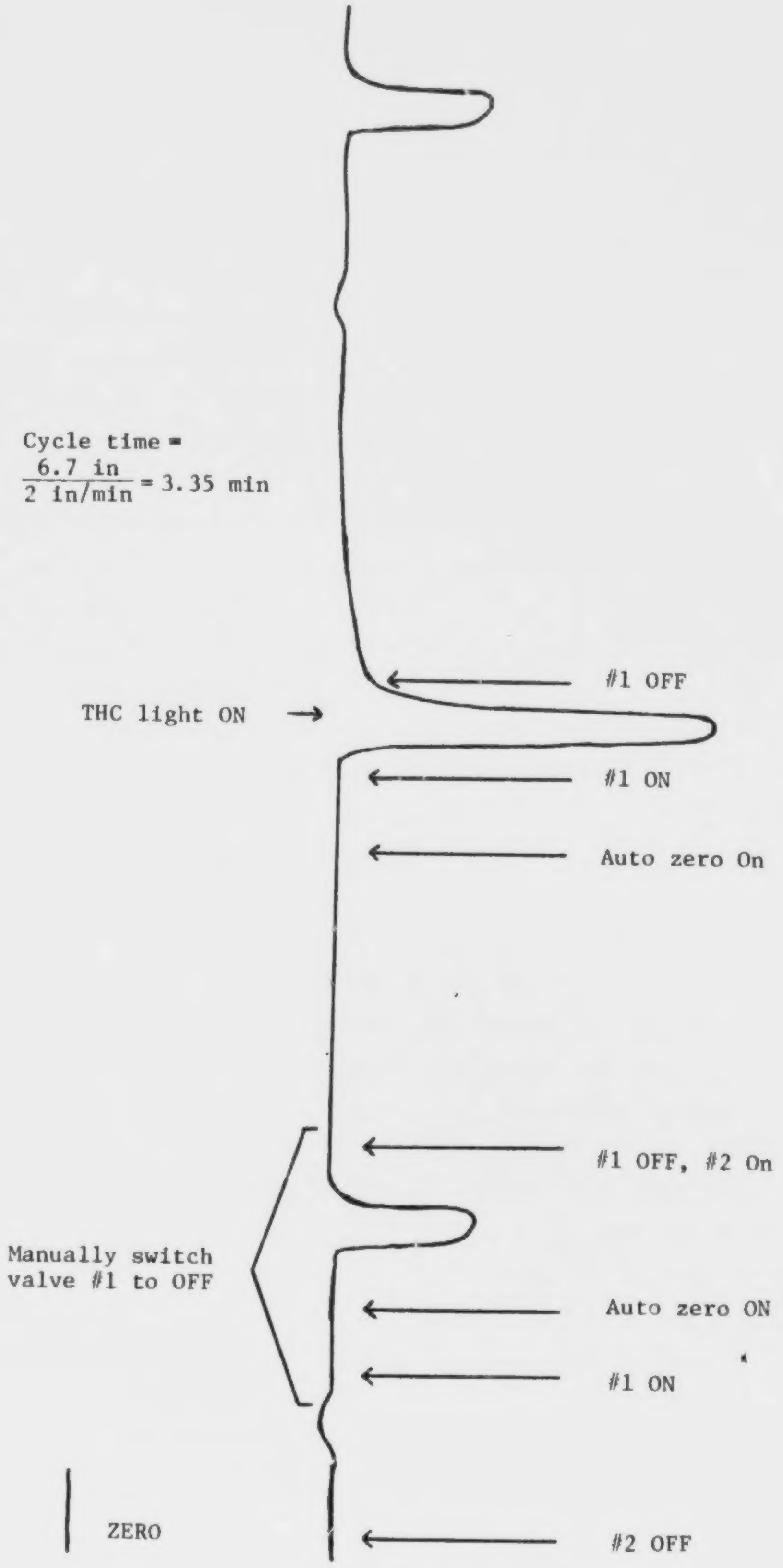

Figure A-3. Calibration cycle for nonmethane hydrocarbon analyzer.

REFERENCES

A-1 Hodgeson, J. A., R. K. Stevens, and B. E. Martin. A Stable Ozone Source Applicable as a Secondary Standard for Calibration of Atmospheric Monitors. Air Quality Instrumentation, Vol. 1, John Scales, ed., 149-150, ISA, Pittsburgh, Pa., 1972.

A-2 40 CFR 50, Appendix D.

A-3 Hodgeson, J. A., R. E. Baumgardner, B. A. Martin, and K. A. Rehme, Stoichiometry and Neutral Iodometric Procedure for Ozone by Gas-Phase Titration with Nitric Oxide. Anal. Chem. 43. 1123-1126, 1971.

APPENDIX B

PERFORMANCE CHARACTERISTICS AND OPERATIONAL SUMMARIES FOR INSTRUMENTS

B-1 Instrument Performance Characteristics

Minimum detectable concentrations, ranges, and precisions for the air quality monitoring instruments used in this study are summarized in Table B-1.

B-2 Operational Summaries for Instruments

Figure B-1 provides an operational summary for each air quality monitoring instrument at each station.

Table B-1. INSTRUMENT PERFORMANCE CHARACTERISTICS

Instrument	Parameter	Minimum Detectable Concentration		Upper Limit		Precision (% of indicated concentration)
		$\mu g/m^3$	ppm	$\mu g/m^3$	ppm	
Bendix Model 8000 Chemiluminescent Ozone Analyzer	O_3	9.8	0.005	392	0.2	
McMillan MEC 1100 Chemiluminescent Ozone Analyzer	O_3	9.8	0.005	980	0.5	
Bendix Model 8101 B Chemiluminescent $NO-NO_2-NO_x$ Analyzer	NO	6.1	0.005	615	0.5	± 0.5
	NO_x		0.005		0.5	± 0.5
	NO_2	9.4	0.005	940	0.5	± 1.0
Bendix Model 8201 Ambient Hydrocarbon Analyzer	THC	53	0.080	6670	10	
	CH_4	93	0.140	6670	10	
	NMHC			6670	10	

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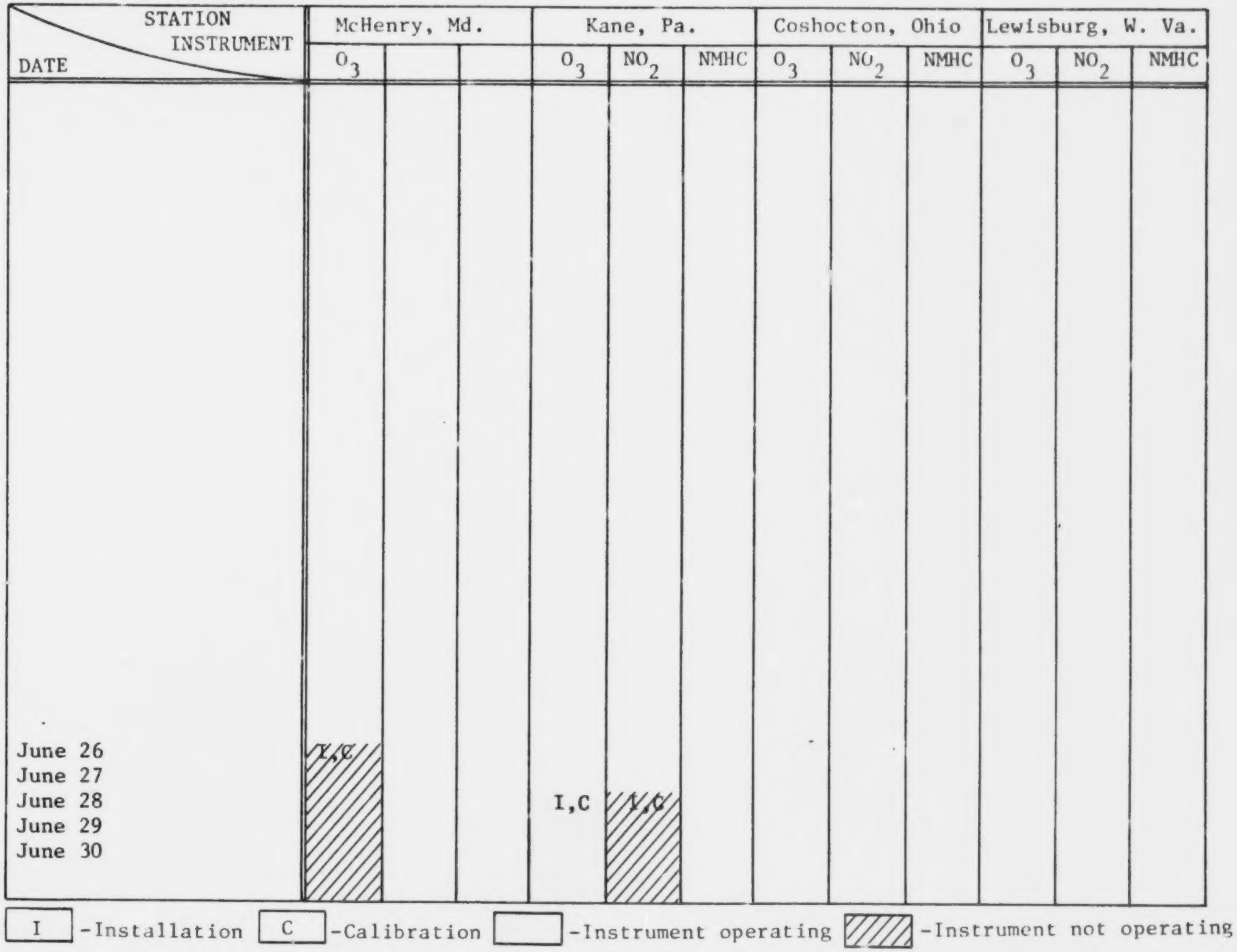

Figure B-1. Operational summary for instruments.

STATION / INSTRUMENT / DATE	McHenry, Md.			Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
	O_3			O_3	NO_2	NMHC	O_3	NO_2	NMHC	O_3	NO_2	NMHC
July 1	▨				▨			I,C				
July 2	▨											
July 3	▨				▨							
July 4	▨				▨							
July 5	▨				▨							
July 6	▨				▨							
July 7	▨				▨							
July 8	▨				▨			▨				
July 9	▨				▨			▨				
July 10	▨				▨			▨				
July 11	▨			C	C			▨				
July 12	▨						I,C	C				
July 13										I,C	I,C	
July 14												
July 15										▨	▨	
July 16										▨	▨	
July 17										▨	▨	
July 18												
July 19												
July 20												
July 21												
July 22												
July 23												
July 24	I,C											
July 25				C	C							
July 26							C	C				
July 27										C	C	
July 28												
July 29												
July 30												
July 31												

I -Installation C -Calibration ☐ -Instrument operating ▨ -Instrument not operating

Figure B-1 (cont.) Operational summary for instruments.

STATION / INSTRUMENT / DATE	McHenry, Md.			Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
	O_3			O_3	NO_2	NMHC	O_3	NO_2	NMHC	O_3	NO_2	NMHC
August 1												I,C
August 2												
August 3												
August 4												
August 5												
August 6												
August 7	C											
August 8				C	C	I,C						
August 9							C	C	I,C			
August 10										C		
August 11										▨	▨	▨
August 12										▨	▨	▨
August 13										▨	▨	C
August 14							▨	▨	▨	I		
August 15												
August 16												
August 17									▨			
August 18												
August 19												
August 20												
August 21	C			C								
August 22					C	C						
August 23							C	C	C			
August 24										C		C
August 25				▨	▨	▨				▨		▨
August 26						▨				▨	C	▨
August 27						▨						
August 28												
August 29										C		
August 30												
August 31						▨						

I -Installation C -Calibration ☐ -Instrument operating ▨ -Instrument not operating

Figure B-1 (cont.) Operational summary for instruments.

STATION / INSTRUMENT / DATE	McHenry, Md.			Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
	O_3			O_3	NO_2	NMHC	O_3	NO_2	NMHC	O_3	NO_2	NMHC
September 1						▨						
September 2						▨						
September 3						▨						
September 4				▨	▨	▨						
September 5				▨	▨	▨						
September 6				C	C	▨						
September 7							C	C	C			
September 8	C											
September 9												
September 10												
September 11						▨						
September 12						▨						
September 13						▨						
September 14				▨	▨	▨	▨					
September 15				▨	▨	▨	▨					
September 16				▨	▨	▨	▨					
September 17				▨	▨	▨	▨	C	C			
September 18				C		▨	C					
September 19					C	C						
September 20	C									C	C	C
September 21						▨						
September 22						▨				C		
September 23						▨				C		
September 24						▨						
September 25												
September 26												
September 27												
September 28												
September 29												
September 30												

I -Installation C -Calibration ☐ -Instrument operating ▨ -Instrument not operating

Figure B-1 (cont.) Operational summary for instruments.

STATION / INSTRUMENT / DATE	McHenry, Md.			Kane, Pa.			Coshocton, Ohio			Lewisburg, W. Va.		
	O_3			O_3	NO_2	NMHC	O_3	NO_2	NMHC	O_3	NO_2	NMHC
October 1												
October 2	C											
October 3				C	C	C						
October 4							C	C	C			
October 5										C		
October 6												
October 7												
October 8												
October 9												
October 10												
October 11												
October 12												
October 13												
October 14												
October 15												
October 16				C		C				C	C	C
October 17					C							
October 18												
October 19												
October 20												
October 21												
October 22												
October 23												
October 24						▨						
October 25						▨						
October 26						▨						
October 27						▨						
October 28						▨						
October 29				C	C	▨						
October 30						▨						
October 31				C	C	▨						

I -Installation C -Calibration ☐ -Instrument operating ▨ -Instrument not operating

Figure B-1 (cont.) Operational summary for instruments.

APPENDIX C

HYDROCARBON ANALYSIS OF GRAB SAMPLES

This appendix presents the results of gas chromatographic analyses of grab samples performed by the Chemistry and Physics Laboratory, National Environmental Research Center, Research Triangle Park, North Carolina.

C-1 Analytical Results

The stations, dates, and times at which grab samples were collected, the dates and times at which they were analyzed, and a sample code designation are shown in Table C-1. Components comprising the hydrocarbon content of each analyzed sample are given in Table C-2. Each component concentration is given as parts per billion carbon (ppbc). To convert ppbc to $\mu g/m^3$, multiply the component concentration by 0.67.

C-2 EPA Analysts' Comments

"Three gas chromatographic procedures were used to determine hydrocarbon composition. Each individual peak observed has been identified by at least one hydrocarbon species. (The only exceptions are four unknown peaks observed in sample N-8). There is extremely high confidence that the components representing the C_1-C_7 aliphatics are correctly identified as aliphatic hydrocarbons. However, the peaks identified as the C_7-C_{10} aromatics have known retention time interferences from halogenated and oxygenated compounds. Therefore, the confidence of the correct identification of the peaks observed on the aromatics chromatogram is not high. Terpene hydrocarbons such as α- and β-pinene have retention times in the region of some of the aromatic peaks.

"The component indicated by the asterisk in Table C-2 is most probably acetaldehyde. This species is indicated by the peak geometry. Acetaldehyde and 2-Methylbutene-2 have similar retention times. However, the acetaldehyde peak tails severely while the corresponding olefin does not. Acetaldehyde has been identified in the urban atmosphere and is a photochemically produced oxygenate of irradiated urban air.

"The very high concentration of the ethylene observed in samples N-1 through N-6 is an indication of ethylene pollution of the nearby

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ambient air by the exhaust of the ethylene-ozone chemiluminescent analyzer. Samples N-6 through N-8 are the usual levels of ethylene in rural ambient air.

"The C_2-C hydrocarbons are observed in most rural air samples. The higher concentration of the C_4-C_5 paraffins in some of the samples would indicate a local source such as the gasoline evaporative emissions from a nearby automobile.

"The very high concentration of toluene is difficult to explain. A nearby source is expected. Interfering halogenates or oxygenates having similar retention times as toluene are not known. The analyst doubts that natural sources of an unidentified component having a similar retention time as toluene could explain the magnitude of the peak.

"The acetylene/CO ratio is somewhat consistent in the samples with the exception of sample N-8. Since it is difficult to imagine any other component having a similar retention time to acetylene on the silica gel column, the acetylene must have come from some nearby source such as an acetylene torch.

"When samples are collected in Tedlar bags, care must be taken not to expose the outside surface of the bags to high concentration of any hydrocarbon component or solvent. The 2 mil thickness of Tedlar is permeable to most of these components."

Table C-1. GRAB SAMPLES COLLECTED FOR HYDROCARBON ANALYSIS

STATION	DATE AND TIME OF SAMPLE COLLECTION	DATE AND TIME OF SAMPLE ANALYSIS	CODE DESIGNATION
Lewisburg, W. Va.	10-16-73 1400-1420	10-18-73 1400	N1
Kane, Pa.	10-17-83 1015-1040	10-18-73 1500	N2
Kane, Pa.	10-17-73 1045-1115	10-18-73 1600	N3
Lewisburg, W. Va.	10-16-73 1215-1250	10-19-73	N4
Coshocton, Ohio	10-4-73 1100-1150	10-11-73 1530	N5
Lewisburg, W. Va.	10-5-73 1300-1380	10-12-73 1300	N6
McHenry, Md.	10-2-73 1300-1330	10-12-73 1400	N7
Coshocton, Ohio #1	10-24-73 1200	10-26-73 1330	N8
Coshocton, Ohio #2	10-24-73 1200	10-26-73 1430	N9

Table C-2. HYDROCARBONS IDENTIFIED IN GRAB SAMPLES

SAMPLE	CONCENTRATION in ppbc (vol./vol.)								
COMPOUND	N-1	N-2	N-3	N-4	N-5	N-6	N-7	N-8	N-9
Ethane	10.3	10.2	14.7	7.3	36.4	13.4	6.8	31.4	34.8
Ethylene	133.0	97.4	172.6	275.0	196.9	375.0	4.5	7.0	8.7
Propane	5.7	6.5	11.0	5.4	26.4	17.6	4.7	18.0	19.3
Acetylene	4.0	4.1	5.9	3.7	3.9	2.2	3.2	63.0	11.5
Isobutane	2.1	3.3	5.8	4.2	9.9	11.3	9.1	20.3	14.1
n-Butane	8.5	8.9	21.7	14.7	30.0	45.2	74.0	61.4	42.4
Propylene	2.0	2.5	1.7	0.2	0.5	1.1	0.7	0.5	0.8
iso-Butylene	2.2	2.4	2.7	1.1	1.3	3.9	3.0	6.4	4.5
trans-Butene-2 Methyacetylene	1.3	1.0	1.3	0.2	1.3	2.0	1.5	4.4	3.0
cis-Butene-2	0.7	0.7	0.8		0.6	1.0	1.0	2.0	1.2
iso-Pentane	8.2	8.1	19.7	17.7	33.1	55.8	126.2	55.2	35.6
n-Pentane	3.8	3.7	8.3	7.2	12.4	27.3	26.0	20.6	18.8
Pentene-1	0.0	0.0	1.1	0.9	0.7	1.6	1.4	1.0	0.8
2-Methylbutene-1	0.0	0.0	1.1	1.0	0.9	1.2	1.2	1.7	1.0
trans-Pentene-2	0.0	0.0	1.4	1.0	1.1	3.2	2.2	3.8	1.6
cis-Pentene-2	0.0	0.0	2.0			2.6	10.0	2.6	0.6
2-Methybutene-2	7.9	4.0*	2.1		3.1	2.4	4.0	4.0	1.3
Cyclopentane 2-Methylpentane	3.8	3.4	9.9	8.0	12.3	41.6	33.6	21.9	14.7
3-Methylpentane	2.1	1.4	4.3	2.5	3.4	19.0	9.3	7.6	5.4
Hexane	2.8	2.1	5.1	2.7	6.2	19.5	8.0	9.3	6.4
2,4-Dimethylpentane					1.0	3.0	>11.2		>8.0
Methycyclopentane					1.3	8.5		>12.0	
1 cis 3 Dimethyl-cyclopentane							4.6		
2,2,4 Trimethyl-pentane						11.7	19.9	4.9	
Trans 3 Dimethyl-cyclopentane							4.7		
Toluene		53.2	189.9	219.2		117.5	1850.0	255.6	935.2

Table C-2. HYDROCARBONS IDENTIFIED IN GRAB SAMPLES (cont'd)

SAMPLE	CONCENTRATION in ppbc (vol./vol.)								
COMPOUND	N-1	N-2	N-3	N-4	N-5	N-6	N-7	N-8	N-9
Nonane		10.8	10.0	7.1				13.5	9.8
Ethylbenzene		3.2	1.2	2.1		9.0	4.0	23.7	5.7
p-Xylene		3.0	1.0	2.0		9.6	4.2	6.1	2.9
m-Xylene		10.2	3.4	7.7		23.2	11.2	30.0	10.0
o-Xylene		5.4	1.8	3.5		11.4	6.0	19.0	6.8
n-Decane		7.5	3.4	7.5		7.6	9.2	36.8	11.1
Isopropylbenzene + Styrene								38.9	7.6
n-Propylbenzene		1.1	0.2	1.0		3.2	1.5	16.6	4.3
m+p Ethyltoluene		3.7	1.8	6.7		11.8	5.0	15.3	4.2
1,3,5-Trimethylbenzene		1.0	1.0	1.9		4.4	1.7	8.4	4.8
tert-Buthybenzene + o-Ethyltoluene		0.4	0.5	1.4		3.6	1.2	3.4	1.5
sec-Butylbenzene + 1,2,4-Trimethylbenzene		6.4	4.8	8.4	13.8	7.7	9.2	4.4	
Unknown		2.2	1.4	1.5		2.2	1.8		4.4
1,2,3 Trimethylbenzene		1.7	0.0	1.6					
n-Butylbenzene + p-Diethylbenzene		1.4	0.0	4.2					
Sum of Unknown Peaks								37.0	
Methane	1630.0	1560.0	1550.0	1510.0	1690.0	1510.0	1510.0	1660.0	1730.0
Carbon Monoxide	530.0	440.0	380.0	320.0	378.0	310.0	310.0	430.0	500.0

INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN EASTERN UNITED STATES

Part 2. Quality Assurance Program

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2-1

1.0 INTRODUCTION

Under a program initiated in June, 1973, the Research Triangle Institute conducted an investigation of ozone and ozone precursor concentrations at non-urban locations in the eastern United States (EPA Contract 68-02-1077, RTI Project 41U-848). This was an outgrowth of a field study of atmospheric ozone concentrations conducted in Garrett County, Maryland, and Preston County, West Virginia, during the summer of 1972. Results of the 1972 summer study indicated that transport of ozone rather than local synthesis reaction (i.e., photochemical ozone production) is responsible for the unusually high ozone concentrations observed in this rural, mountainous area. The 1973 summer field program, which consisted of data collection (4 months), analysis, and interpretation, was designed to evaluate the occurrence and extent of high ozone concentrations at nonurban locations. The measurements made at the respective sites were: O_3 - McHenry, Maryland; O_3, NO_2, NMHC - Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia. The purpose of the present study was to conduct a quality assurance program relative to the air quality measurements being conducted under Contract 68-02-1077.

Calibration of instruments is necessary for the successful pursuit of any study in which sample analysis is employed. Calibration of instruments in the field, because of logistic problems, is usually more difficult than calibration in the laboratory. In the above-mentioned study the difficulty was further compounded by having several widely separated field sites at which atmospheric measurements were made.

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In the 1973 summer program, the instruments at each station were calibrated on an orderly biweekly schedule. These calibrations provide a check on accuracy of data and, if the data are accurate, allow a valid comparison of both data and instruments at the various stations. In field studies, however, a back-up system of checks and calibration is always desirable, especially as a test of comparability of data taken simultaneously at different sites.

A quality assurance program was designed to provide a direct test of the comparability of data obtained from the four widely separated monitoring stations. The program was carried out by taking a separate set of ambient air analyzers, calibration system and calibration gases in the RTI Environmental Monitoring Laboratory to each station and sampling from a manifold with an intake common to both the mobile and the fixed station. The instruments in the mobile unit were calibrated by a different team from that performing the scheduled calibration of the fixed stations. Simultaneous sampling was conducted for a minimum of 40 hours at each of the sites. Signals from the instruments in the fixed site and mobile laboratory were recorded simultaneously on the data acquisition and on-line processing system located in the Environmental Monitoring Laboratory.

Thus, the behavior of instruments at each site was compared to the behavior of an additional set of instruments located in the Environmental Monitoring Laboratory which for this study served as a primary standard or reference point for each of the gaseous pollutants being monitored. The Environmental Monitoring Laboratory was equipped with the best available instrumentation for monitoring the pollutants in question. In addition, the equipment was operated, calibrated, and maintained by highly qualified technical personnel, and all calibrations were conducted with extra care under essentially laboratory conditions. In one step this served to verify both the validity of the environmental data being generated at the fixed station and the comparability of data from the various sites. At the same time the precision of a set of similar instruments was checked by running them side by side on a common sample. Analysis of the resulting data provides a quantitative assessment of the individual station's performance and the relationship of the measurements among the four monitoring sites.

A description of the mobile Environmental Monitoring Laboratory and the quality assurance program are presented in Sections 2.0 and 3.0, respectively. Data comparisons, results of statistical analyses, and a summary of results are presented in Sections 4.0, 5.0, and 6.0. The calibration systems and detailed calibration procedures are described in Appendix A. Data for ozone and nitrogen dioxide from the fixed and mobile site analyzers and supplementary data (i.e., sulfur dioxide and hydrocarbons) obtained from analyzers located in the Environmental Monitoring Laboratory are tabulated in Appendix B.

2.0 MOBILE LABORATORY AND EQUIPMENT

2.1 Mobile Monitoring Laboratory

The RTI Environmental Monitoring Laboratory used in this study is a self-contained, 31-foot motorized vehicle custom-built for air quality monitoring. It was outfitted with the latest complement of air quality monitoring instrumentation, a self-contained calibration system for each pollutant analyzer, and a digital magnetic tape recording system coupled to a minicomputer capable of online data processing and printout of real-time air quality data in physical units and storage of the raw data on magnetic tape. The motorized van has a self-contained motor-generator for generation of electrical power; a controlled environment (heating and cooling); an ac voltage regulator; a glass and Teflon manifold system for passage of air samples to the monitors; a tower for mounting various meteorological sensors; and storage space for compressed air and gas tanks.

Two interior views of the vehicle are shown in Figures 1 and 2; exterior views of the mobile unit may be seen in the photographs of the setup at the respective sites.

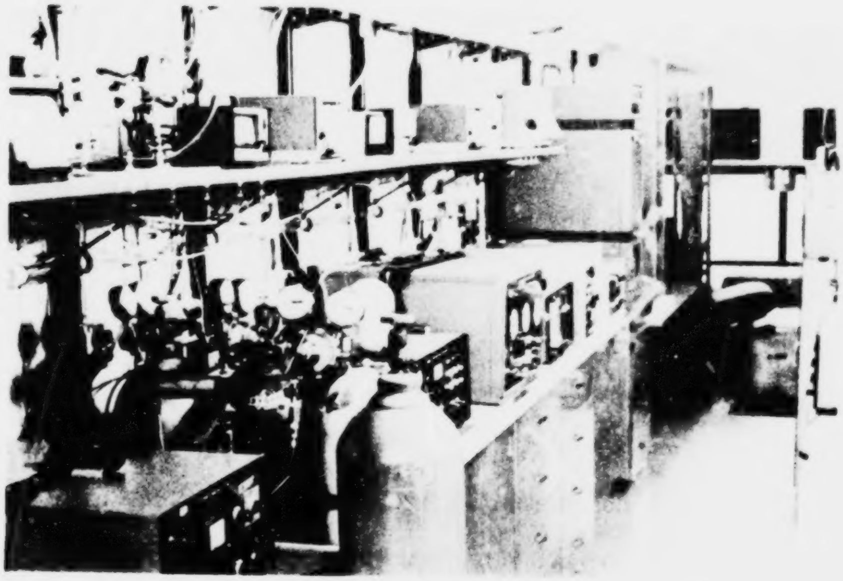


Figure 1. Interior view of Environmental Monitoring Laboratory showing some of the ambient air analyzers.

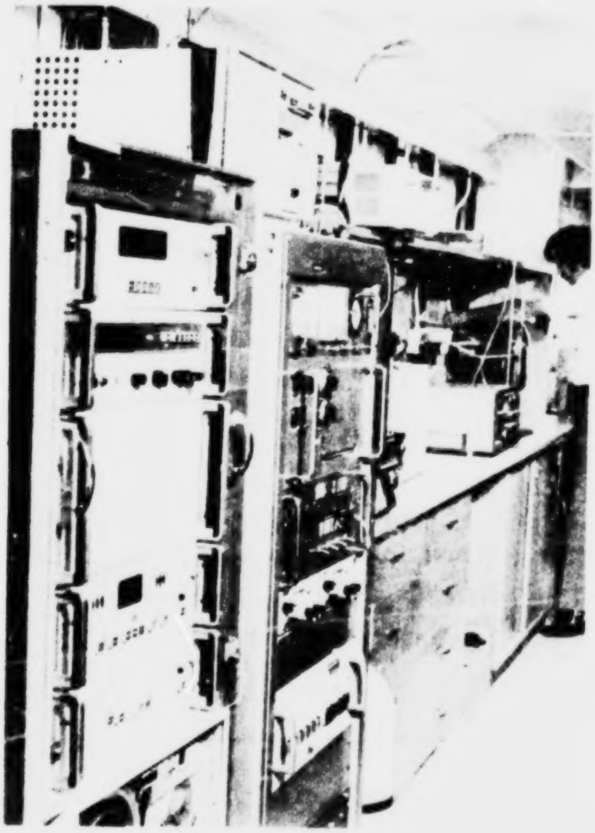


Figure 2. Interior view of Environmental Monitoring Laboratory with data acquisition system in foreground.

2.2 Air Quality Analyzers and Calibration System

For this study, the mobile laboratory was equipped with analyzers capable of continuous measurement of ambient air concentrations of ozone (O_3); oxides of nitrogen (NO_x); (NO), (NO_2); total sulfur (S); carbon monoxide (CO); methane (CH_4); total hydrocarbons (THC); and nonmethane hydrocarbons (NMHC). All air pollutants except NO_2 and NMHC are measured by direct detection. Nitrogen dioxide and NMHC are computed by subtracting NO from NO_x and CH_4 from THC, respectively. Table I gives details for each analyzer.

Table I AIR QUALITY ANALYZERS

Instrumentation	Principle of Detection	Range
Bendix O_3 Model 8002	Gas phase chemiluminescence	0-0.2 ppm
Bendix NO, NO_2, NO_x Model 8101-B	Gas phase chemiluminescence	0-0.5 ppm
RTI O_3 Model 525	Solid phase chemiluminescence	0-0.5 ppm
Bendix Total Sulfur Model 8300	Flame photometry	0-1.0 ppm
Beckman CH_4, CO, THC Model 6800	Flame ionization	0-10.0 ppm
Bendix CH_4, CO, NMHC Model 8201	Flame ionization	0-10.0 ppm
Bendix CO Model 8501-5FA	Nondispersive infrared	0-20.0 ppm

Apparatus and associated equipment utilized in the mobile laboratory for calibration of ambient air quality analyzers included the following: apparatus to perform manual iodometric analyses (neutral buffered KI Method), KI sampling train, spectrophotometer (Spectronic 70), and ultraviolet ozone source; gas phase titration system for producing NO_2 by oxidation of NO to NO_2 with ozone; and certified cylinders of CH_4 and CO in zero air.

The contents of compressed gas cylinders used for calibration purposes and their contents as certified by supplier's analysis are presented in Table II.

Table III presents a synopsis of pollutants measured by instruments carried in the mobile laboratory and methods used for calibration. Included are the precision and accuracy associated with the calibration techniques.

Table II CALIBRATION GASES

Instrument	Cylinder Content	Supplier	Supplier's Analysis
Bendix NO_x	NO in N_2	Scott	50.2 ppm ± 2%
Beckman 6800	CH_4 in Air	Scott	99.6 ppm ± 2%
	CH_4 in Air	Scott	4.64 ppm ± 2%
	CH_4 in Air	Scott	1.6 ppm ± 2%
	CO in Air	Scott	95.9 ppm ± 2%

Table III

CALIBRATION TECHNIQUES

Pollutant	Calibration Technique	Precision/Accuracy of Calibration Method
Ozone	UV-Ozone Generation Referenced to Neutral-Buffered KI Procedure (as published in Federal Register, April 30, 1971 Edition)	Estimated Accuracy.........± 5% Precision of Calibration......± 2%
Nitrogen Dioxide	Gas Phase Titration (as published in Federal Register, June 8, 1973 Edition)	Estimated Accuracy.........± 5% Precision of Calibration......± 2%
Nitric Oxide	Dilution of Standard Cylinder Gas (NO in N_2)	Accuracy of Component Analysis.........± 2% Precision of Calibration......± 2%
Sulfur Dioxide	NBS Permeation Tube	Accuracy...........± 1% Precision of Calibration......± 1%
Carbon Monoxide	Standard Cylinder Gas (CO in Air)	Accuracy of Analysis.........± 2% Precision of Calibration......± 2%
Methane Total Hydrocarbons	Standard Cylinder Gas (CH_4 in Air)	Accuracy of Analysis.........± 2% Precision of Calibration......± 2%

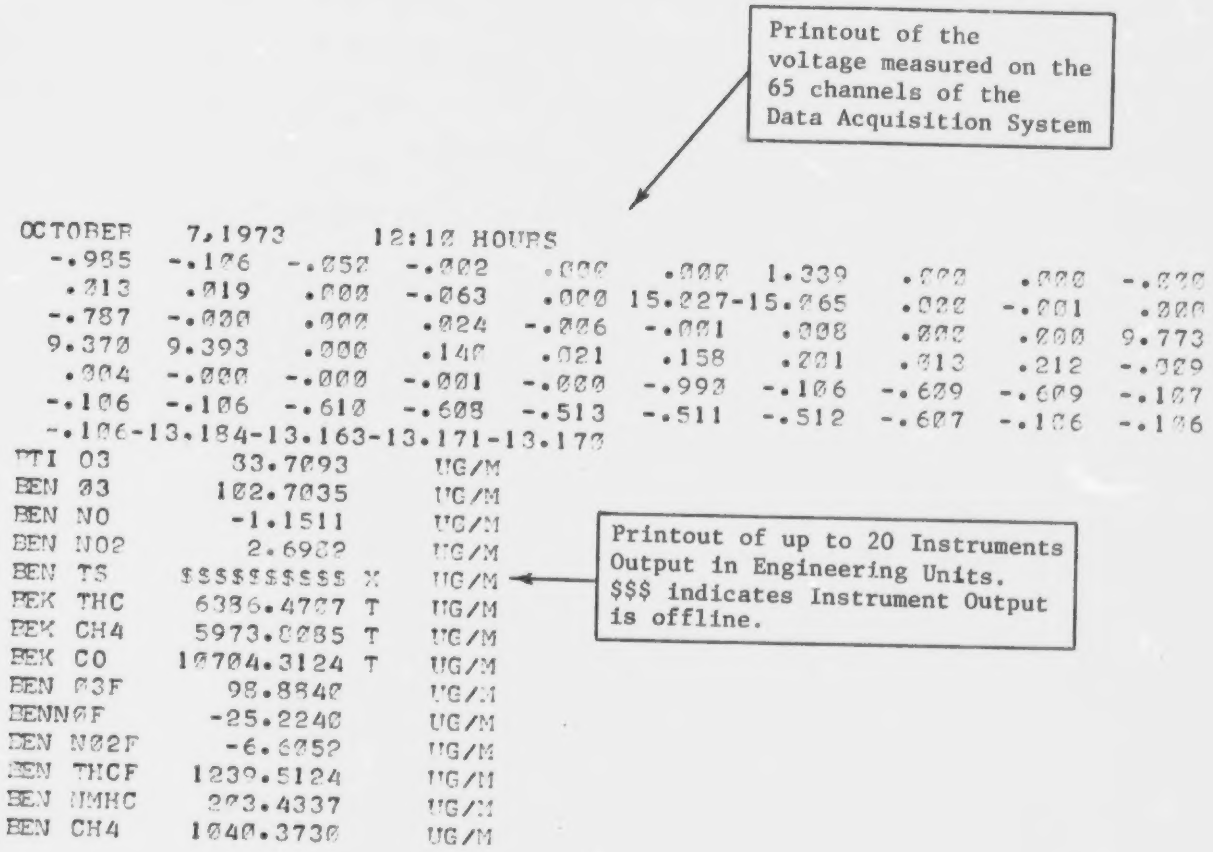
2.3 Data Acquisition System

The Environmental Monitoring Laboratory data system consists basically of a digital magnetic tape data acquisition system and a minicomputer. The signals from the respective analyzers are scanned at five-minute intervals. These sampled voltages are digitized and recorded on the magnetic tape in computer compatible format; in addition, the scanned data are introduced into the minicomputer where the appropriate transfer functions are applied to each of the analyzer signals and the resulting values in physical units are printed out. An example of the data output for a five-minute scan is shown in Figure 3. The five-minute data are accumulated and at the end of each hour a summary which includes the five-minute data plus the hourly average is printed out as shown in Figure 4.

The output signals from the respective analyzers in the fixed station were coupled into the mobile laboratory data system so that all signals were sampled and recorded by a common system. This was accomplished by running a multiple-pair shielded cable from the mobile laboratory to the fixed site station and picking up the signals at the input to fixed station magnetic tape recording unit.

The system is so designed that all operating mode information and calibration values may be entered into the system by digital mode switches and via the teleprinter keyboard, respectively. Any changes in instrument status are automatically compiled and calibration information (i.e., transfer functions) is also updated automatically via the minicomputer.

Backup data recording equipment consists of strip-chart recorders for each of the analyzer outputs and a digital printer which prints out the same data that are recorded on magnetic tape.

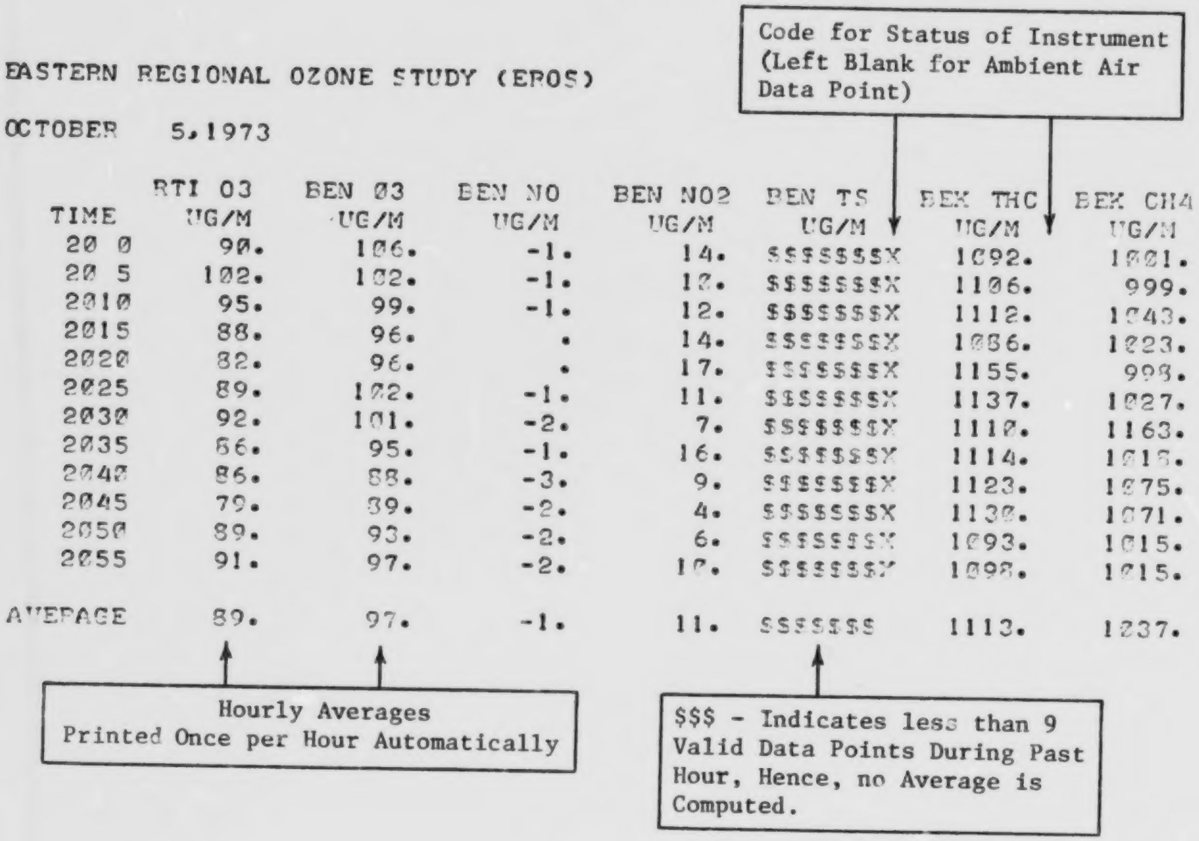


Printout of the voltage measured on the 65 channels of the Data Acquisition System

```
OCTOBER    7,1973       12:10 HOURS
   -.985   -.106   -.052   -.002    .000    .000  1.339    .000    .000   -.000
    .013    .019    .000   -.063    .000 15.227-15.065    .020   -.001    .000
   -.787   -.000    .000    .024   -.006   -.001    .008    .002    .000   9.773
   9.370   9.393    .000    .140    .021    .158    .201    .013    .212   -.029
    .004   -.000   -.000   -.001   -.000   -.992   -.106   -.609   -.609   -.107
   -.106   -.106   -.610   -.608   -.513   -.511   -.512   -.607   -.106   -.106
   -.106-13.184-13.163-13.171-13.173
 PTI 03         33.7093        UG/M
 BEN 03        102.7035        UG/M
 BEN NO         -1.1511        UG/M
 BEN NO2         2.6982        UG/M
 BEN  TS    $$$$$$$$$$ X       UG/M
 BEK  THC     6386.4707 T      UG/M
 BEK  CH4     5973.0085 T      UG/M
 BEK  CO     10704.3124 T      UG/M
 BEN  03F       98.8840        UG/M
 BENN0F        -25.2240        UG/M
 BEN  N02F      -6.6052        UG/M
 BEN  THCF    1239.5124        UG/M
 BEN  NMHC     203.4337        UG/M
 BEN  CH4     1040.3730        UG/M
```

Printout of up to 20 Instruments Output in Engineering Units. $$$ indicates Instrument Output is offline.

Figure 3. Sample data output for five-minute scan.



```
EASTERN REGIONAL OZONE STUDY (EROS)

OCTOBER   5,1973

           RTI O3   BEN O3    BEN NO    BEN NO2  BEN TS    BEX THC   BEX CH4
 TIME       UG/M     UG/M      UG/M      UG/M    UG/M      UG/M      UG/M
  20 0       90.      106.      -1.       14.   $$$$$$$X   1092.     1001.
  20 5      102.      102.      -1.       10.   $$$$$$$X   1106.      999.
  2010       95.       99.      -1.       12.   $$$$$$$X   1112.     1043.
  2015       88.       96.        .       14.   $$$$$$$X   1086.     1023.
  2020       82.       96.        .       17.   $$$$$$$X   1155.      998.
  2025       89.      102.      -1.       11.   $$$$$$$X   1137.     1027.
  2030       92.      101.      -2.        7.   $$$$$$$X   1110.     1163.
  2035       86.       95.      -1.       16.   $$$$$$$X   1114.     1018.
  2040       86.       88.      -3.        9.   $$$$$$$X   1123.     1075.
  2045       79.       89.      -2.        4.   $$$$$$$X   1130.     1071.
  2050       89.       93.      -2.        6.   $$$$$$$X   1093.     1015.
  2055       91.       97.      -2.       10.   $$$$$$$X   1098.     1015.

AVERAGE      89.       97.      -1.       11.   $$$$$$$    1113.     1237.
```

Code for Status of Instrument (Left Blank for Ambient Air Data Point)

Hourly Averages
Printed Once per Hour Automatically

$$$ - Indicates less than 9 Valid Data Points During Past Hour, Hence, no Average is Computed.

Figure 4. Sample data output for hourly summary.

3.0 FIELD QUALITY ASSURANCE PROGRAM

3.1 Procedure

The purpose of the program was to conduct a quality assurance program relative to the air quality measurements being made at the four stations operated under the referenced Contract. The specific locations and respective site descriptions are given in Section 3.2. The pollutants measured in the four stations were O_3, NMHC, and NO_2. Operation of the network consisted of daily checks by local personnel at each station and biweekly maintenance and calibration of all analyzers by contractor personnel. A single portable calibration system was utilized throughout to calibrate all O_3 and NO_2 analyzers during this study. Continuity was maintained throughout the measurement program by using a single calibration system and operator. The quality assurance program was designed to provide a direct test of the comparability of the data obtained from the four widely separated monitoring stations, within the constraints of time and funds.

The mobile air monitoring laboratory described in Sections 2.1 and 2.2 was used in this quality assurance program. The program was conducted over a relatively short period of time in order that the personnel and the techniques they utilized would have minimal variability. Consideration was given to the type of data, number of samples, period of comparison, and calibration sequence in establishing the general field procedure presented in Figure 5. The time indicated for each segment in the schedule is the approximate time allocated for equipment warm-up, calibration, and comparison and data acquisition, both prior to and after calibration of the fixed site analyzers.

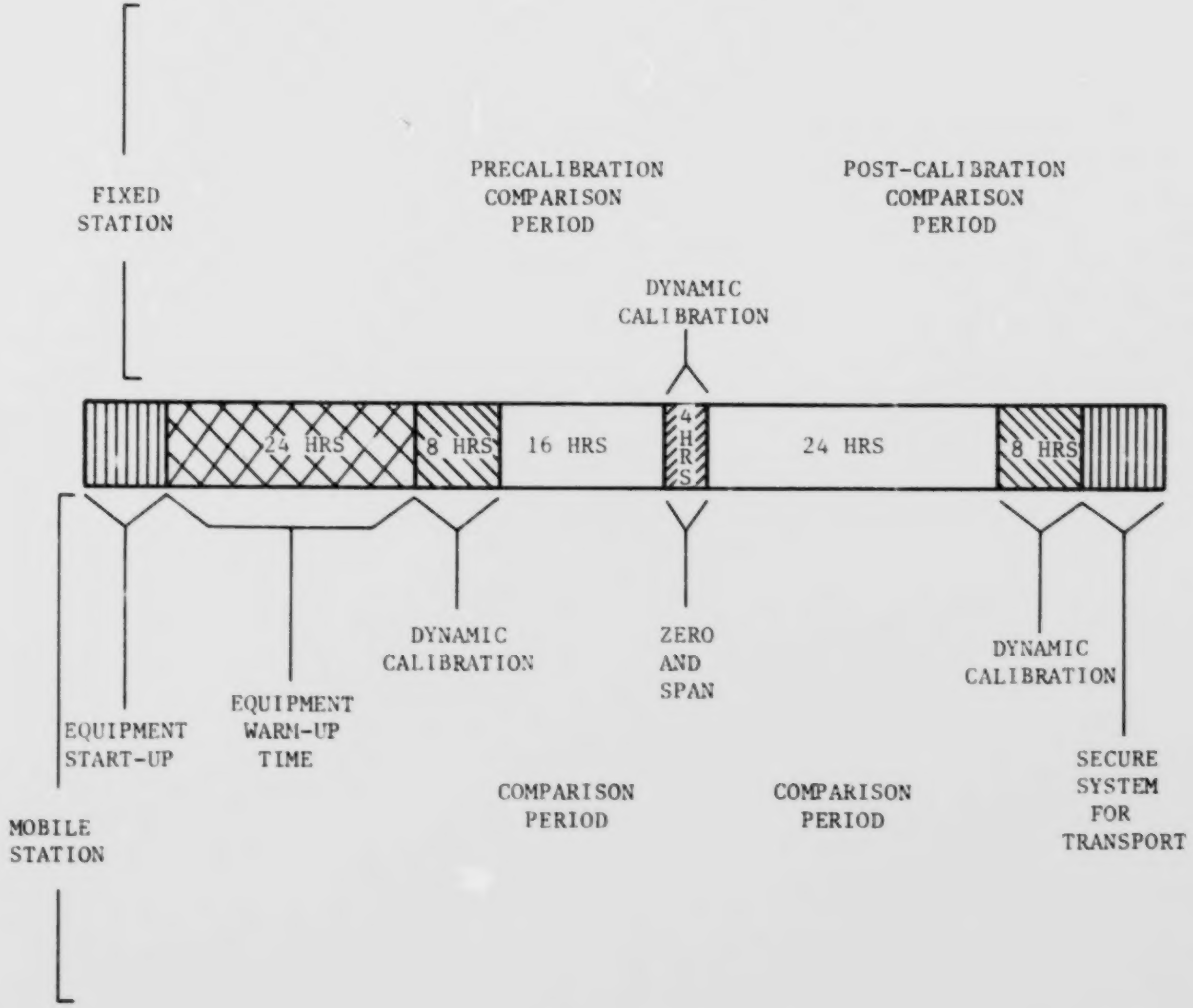

FIXED STATION
PRECALIBRATION COMPARISON PERIOD
POST-CALIBRATION COMPARISON PERIOD
DYNAMIC CALIBRATION
24 HRS
8 HRS
16 HRS
4 HRS
24 HRS
8 HRS
EQUIPMENT START-UP
EQUIPMENT WARM-UP TIME
DYNAMIC CALIBRATION
ZERO AND SPAN
DYNAMIC CALIBRATION
SECURE SYSTEM FOR TRANSPORT
COMPARISON PERIOD
COMPARISON PERIOD
MOBILE STATION

Figure 5. General procedure schedule for air quality assurance program

The site visitation schedule was as follows:

August 27-30, 1973 -- Lewisburg, West Virginia
September 5-7, 1973 -- Kane, Pennsylvania
September 14-18, 1973 -- Coshocton, Ohio
September 21 - October 3, 1973 -- McHenry, Maryland
October 5-7, 1973 -- Lewisburg, West Virginia

A more detailed presentation of the sampling times and order of events is given in Section 3.3.

3.2 Location and Description of Sites

Lewisburg, West Virginia

The Lewisburg site was located immediately adjacent to Greenbrier Valley Airport near Lewisburg, West Virginia. Elevation above mean sea level is approximately 705 m (2301 ft.). The fixed site station was a portable laboratory owned and operated by the Bendix Corporation. It was located on a hill overlooking the airport. Exposure to the air was good in all directions. Figure 6 shows the environmental monitoring laboratory at the Lewisburg location and the arrangement of the sampling inlets.

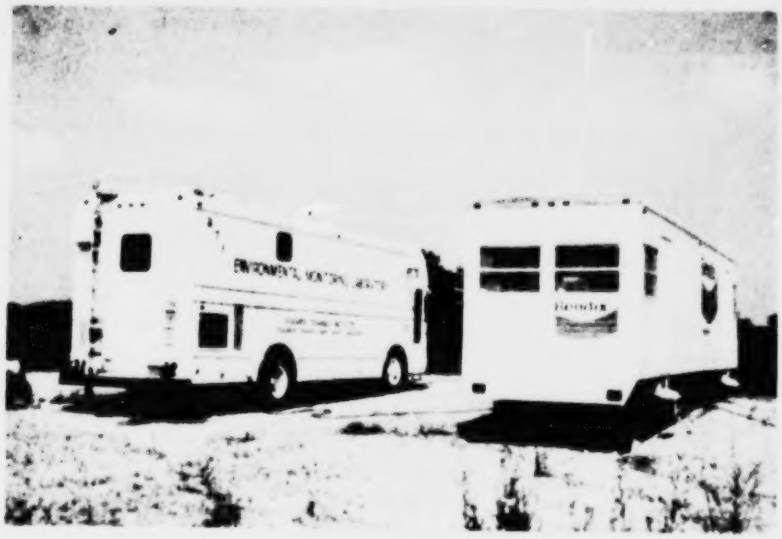


Figure 6. Lewisburg, West Virginia site.

Kane, Pennsylvania

The northernmost station was located in Kane, Pennsylvania. The borough of Kane is surrounded on three sides by the Allegheny National Forest. The specific location of the fixed station was the industrial arts room of the Kane Area Senior High School. The school is situated at the highest point in the area, 630 m (2060 ft.) above mean sea level. Initially, instrumentation was located on tables inside the industrial arts room; after school started in the fall, the equipment was moved to an EPA supplied mobile van just outside the industrial arts room (in the far right-hand part of Figure 7). The air inlet was at a point 1.8 m (6 ft.) above the building roofline and was at the same point for both periods. The mobile laboratory was parked immediately next to the building and a Teflon sampling line attached to the entry port of the fixed station (see Figure 7).

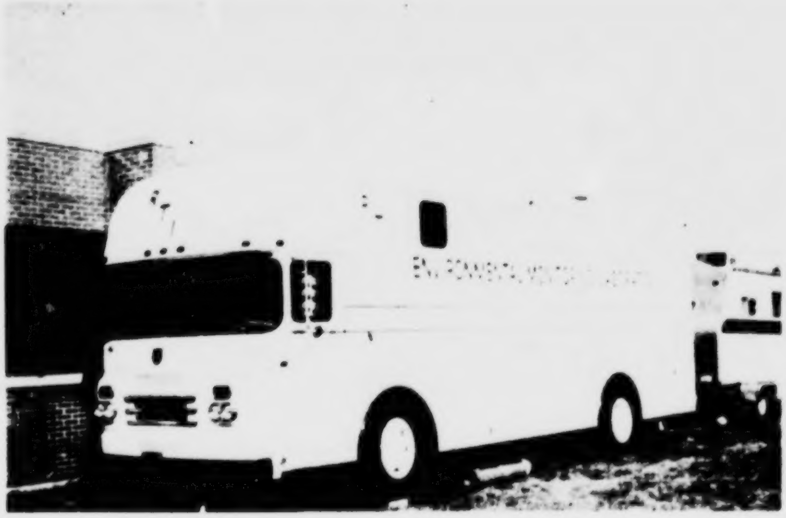


Figure 7. Kane, Pennsylvania, site.

Coshocton, Ohio

The Coshocton site was located at the North Appalachian Experimental Watershed facilities near Coshocton, Ohio. The complex of buildings is 354 m (1160 ft.) above mean sea level. The acreage surrounding the station is used mainly for farming. There are no obstructions to air movement. The fixed station was located in a room on the second floor of a structure known as the engineering building. It was not possible to bring the mobile laboratory as close to the fixed station as was desired. In order to sample air from the same inlet as the fixed station, a 1 inch O. D. Teflon line was mounted on a cable as shown in Figure 8.

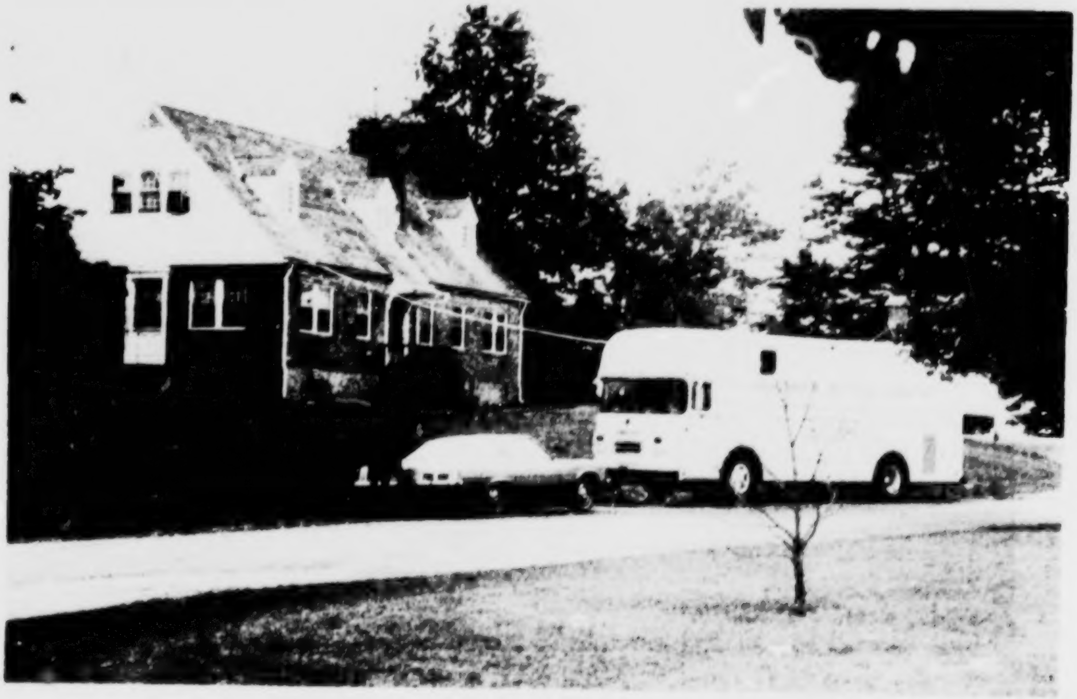


Figure 8. Coshocton, Ohio site.

Garrett County Airport, McHenry, Maryland

The Garrett County Airport is at an elevation of approximately 885 m (2900 ft.) above mean sea level. The site provided excellent exposure for ambient air monitoring instruments. The only pollutant measured at the fixed site was ozone. The ozone monitor, strip-chart recorder, and data acquisition system were located in a small workroom at the east end of the hangar. It was possible to position the mobile laboratory quite close to the fixed site. A short length of Teflon tubing connected the instruments in the mobile unit to the ambient air inlet point. This arrangement is shown in Figure 9.

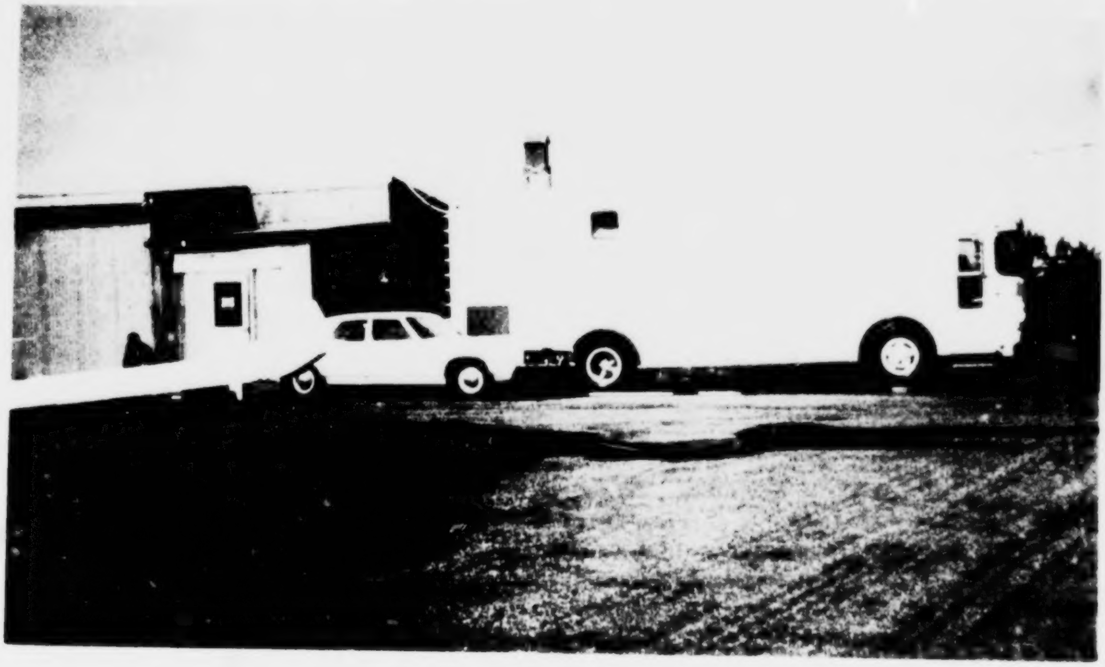


Figure 9. Garrett County Airport, McHenry, Maryland site.

3.3 Summary of Data Acquisition at Each Site

At the time of the mobile laboratory visits, each of the fixed sites had been in operation for at least six weeks; thus, several biweekly calibrations had been performed. Figure 10 summarizes the times of data acquisition by the fixed stations as well as the dates of the mobile laboratory/fixed site comparison periods.

Lewisburg, West Virginia, was the first site visited. The Kane, Coshocton, and McHenry sites were then visited in that order. The visit to Garrett County was the longest; part of this period was one of unattended operation of the mobile laboratory and fixed site. A second, short visit was made to Lewisburg to re-examine a hydrocarbon analyzer which malfunctioned during the first visit. Figures 11, 13, 15, 17a, 17b and 21 in Section 4 show in more detail the events that occurred during the comparison periods.

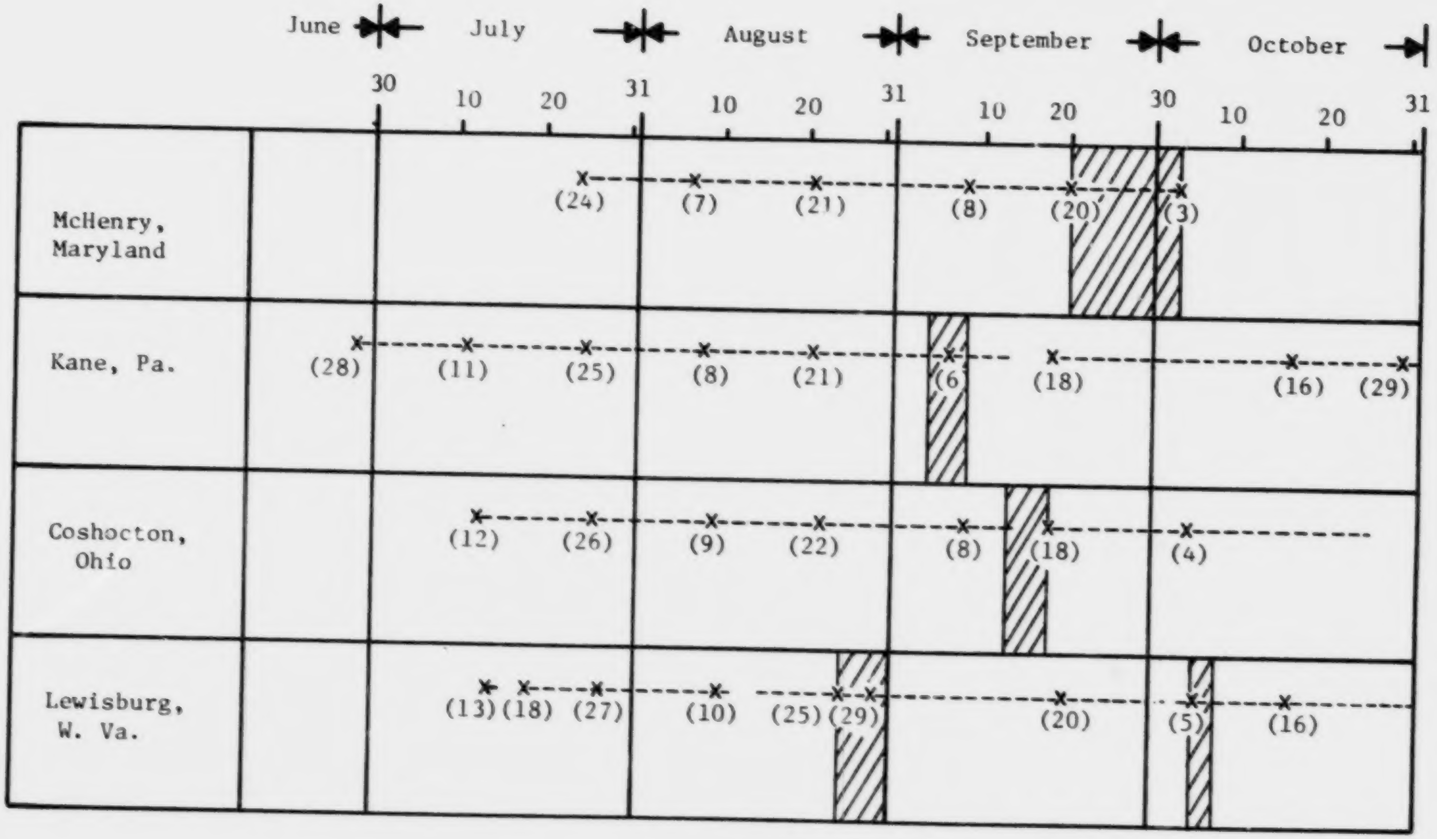


Figure 10. Data Collection and Calibration Dates; Mobile Lab Comparison Periods. Rural Oxidant Study

4.0 DATA COMPARISON

As was stated in Section 3.1, the pollutants measured for comparison were O_3, NMHC, and NO_2. Examination of the fixed site data indicated that, except for brief excursions, the NO_2 levels were very low; in fact, near the limit of detectability of the chemiluminescent analyzer. In the case of nonmethane hydrocarbons (NMHC), the Bendix 8201 Hydrocarbon Analyzers at the fixed site suffered from a positive moisture interference in the total hydrocarbon (THC) measurement which affected the NMHC values. This interference was discovered, confirmed during the comparison period, and later corrected. Thus, no data exist for comparison between hydrocarbon measurements from the mobile laboratory and fixed sites.

For the above reasons, the data comparison and statistical analysis of the NO_2 and NMHC measurements are not presented. The following sections will be concerned with comparison of ozone data. Figures showing detailed calibration and comparison periods at each site and graphical comparisons of the O_3 concentration during the same periods are presented in Sections 4.1 to 4.5.

On some of the graphical presentations a third plot is drawn representing the O_3 concentration from the fixed site analyzer as recorded by the Westinghouse Pulse-O-Matic data acquisition system located at the fixed site. In most instances these concentrations "track" quite well with the O_3 concentration computed by the Mobile Laboratory's data acquisition system and computer. It should be pointed out that the two systems collect data in different manners. The Westinghouse system integrates the signal from the fixed O_3 analyzer for a fifteen minute interval. The

Hewlett-Packard system aboard the mobile laboratory collects an instantaneous value every five minutes; the averaging time is essentially the response time of the analyzer; a fifteen minute value would be the average of three such values. Because of this difference in data collection methods, small variations would be expected for fifteen minute averages, hourly averages, and daily averages.

4.1 LEWISBURG, WEST VIRGINIA (August 25-31, 1973)

The first site visited by the mobile laboratory during the comparison study was Lewisburg, West Virginia. Figure 11 is the first of a group of figures that show chronologically the events that occurred during the comparison of instrument performance in both the mobile and fixed stations. In general, the activities at the fixed site are listed on the left; those of the mobile laboratory on the right of the time column. Within the time column, calibration periods are indicated by cross-hatching: mobile laboratory, right slanted; and fixed station, left slanted.

The warmup period for the mobile site instruments began on the evening of August 26. Due to problems associated with the line voltage regulation system, the comparison period began somewhat later, on the evening of August 28.

Both the fixed and mobile site analyzers were calibrated on the afternoon and evening of August 29. A second comparison period followed, this time after dynamic multipoint calibration of both the fixed and mobile analyzers.

The ozone analyzer in the mobile laboratory underwent a zero and span operation at 0930 on August 30. The transfer equation changed slightly, so a third comparison period for O_3 analyzers began from this point until all analyzers went offline at 0915 on August 31 and the comparison period ended.

Figure 12 presents graphically the comparison between the ozone analyzers at the fixed and mobile sites before and after the calibration periods mentioned above. Based on hourly averages, the fixed site ozone analyzer indicated slightly higher ozone concentrations than those from

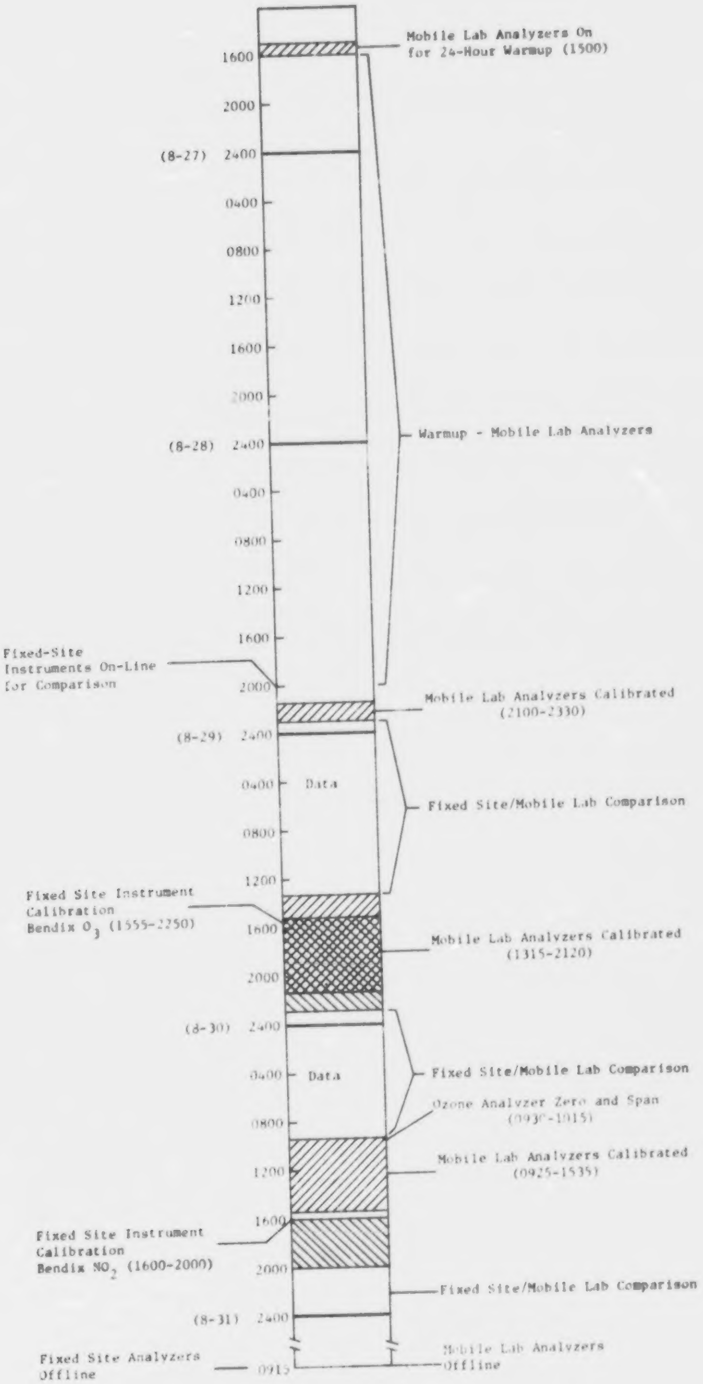

Mobile Lab Analyzers On for 24-Hour Warmup (1500)
1600
2000
(8-27) 2400
0400
0800
1200
1600
2000
Warmup - Mobile Lab Analyzers
(8-28) 2400
0400
0800
1200
1600
Fixed-Site Instruments On-Line for Comparison
2000
Mobile Lab Analyzers Calibrated (2100-2330)
(8-29) 2400
0400
Data
Fixed Site/Mobile Lab Comparison
0800
1200
Fixed Site Instrument Calibration Bendix O_3 (1555-2250)
1600
Mobile Lab Analyzers Calibrated (1315-2120)
2000
(8-30) 2400
0400
Data
Fixed Site/Mobile Lab Comparison
Ozone Analyzer Zero and Span (0930-1015)
0800
Mobile Lab Analyzers Calibrated (0925-1535)
1200
1600
Fixed Site Instrument Calibration Bendix NO_2 (1600-2000)
2000
Fixed Site/Mobile Lab Comparison
(8-31) 2400
Fixed Site Analyzers Offline
0915
Mobile Lab Analyzers Offline

Figure 11. Fixed Site/Mobile Lab Comparison
August 27 - September 1, 1973
Lewisburg, W. Va.

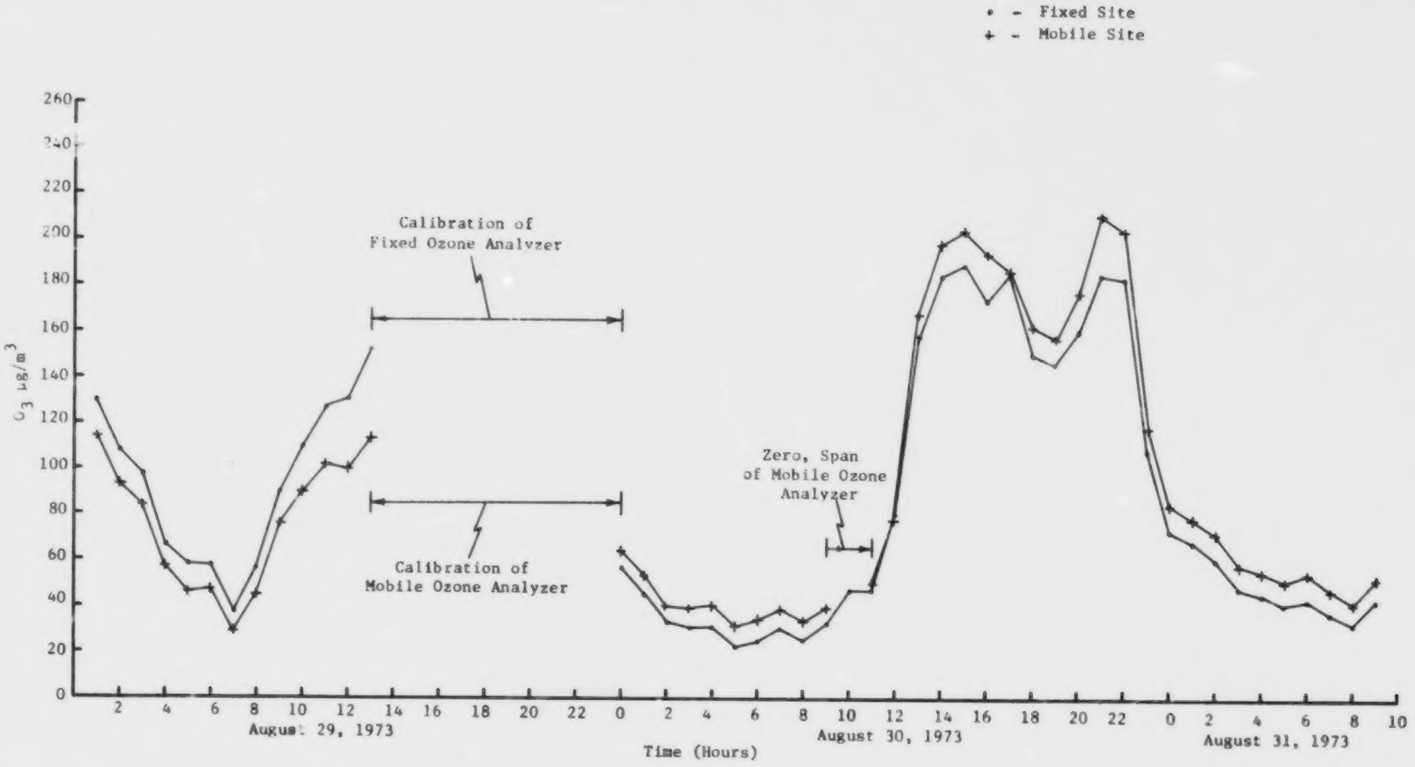


Figure 12. Quality Assurance Program
Lewisburg, W.Va.
August 29, 30, 31, 1973

the mobile site ozone analyzer. After calibration of both analyzers, the ozone concentrations from the fixed site were slightly below those indicated by the mobile site.

The Beckman 6800 Air Quality Chromatograph located in the mobile site was not operational during the period August 25-31, 1973, thus requiring a second comparison period for Lewisburg. The abnormally high nonmethane hydrocarbon values obtained with the Bendix 8201 Hydrocarbon Analyzer raised questions with regards to accuracy and validity of the data from the analyzers. An interference was suspected and the manufacturer was asked to investigate the problem.

4.2 KANE, PENNSYLVANIA (September 4-8, 1973)

The second site visited during the comparison study was Kane, Pennsylvania. The warmup period for the mobile site analyzers began at 1200 on September 4, 1973, and the comparison periods before and after fixed site calibrations extended from 2300 on September 5, 1973, to 1200 on September 6, 1973, and from 0100 on September 7, 1973, to 0800 on September 8, 1973, respectively. Final calibration of the mobile site analyzers was completed at 1030. (See Figure 13.)

Figure 14 indicates that the fixed site ozone analyzer measurements were somewhat less than those indicated by the mobile site ozone analyzer both before and after calibration.

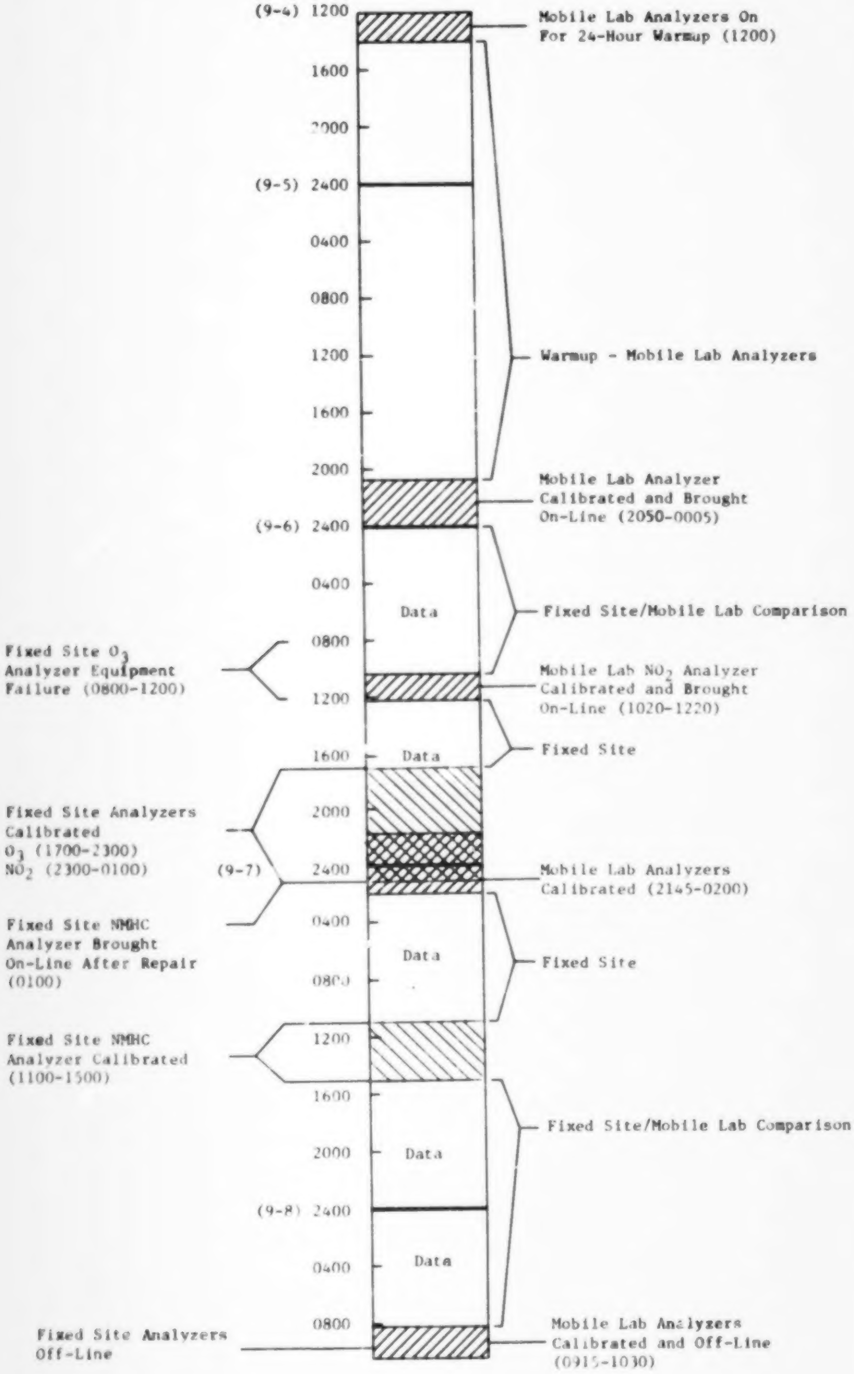

(9-4) 1200
Mobile Lab Analyzers On For 24-Hour Warmup (1200)
1600
2000
(9-5) 2400
0400
0800
1200
Warmup - Mobile Lab Analyzers
1600
2000
Mobile Lab Analyzer Calibrated and Brought On-Line (2050-0005)
(9-6) 2400
0400
Data
Fixed Site/Mobile Lab Comparison
0800
Fixed Site O_3 Analyzer Equipment Failure (0800-1200)
Mobile Lab NO_2 Analyzer Calibrated and Brought On-Line (1020-1220)
1200
1600
Data
Fixed Site
Fixed Site Analyzers Calibrated O_3 (1700-2300) NO_2 (2300-0100)
2000
(9-7) 2400
Mobile Lab Analyzers Calibrated (2145-0200)
Fixed Site NMHC Analyzer Brought On-Line After Repair (0100)
0400
Data
Fixed Site
0800
Fixed Site NMHC Analyzer Calibrated (1100-1500)
1200
1600
Fixed Site/Mobile Lab Comparison
2000
Data
(9-8) 2400
0400
Data
0800
Fixed Site Analyzers Off-Line
Mobile Lab Analyzers Calibrated and Off-Line (0915-1030)

Figure 13. Fixed Site/Mobile Lab Comparison
September 4-8, 1973
Kane, Pennsylvania

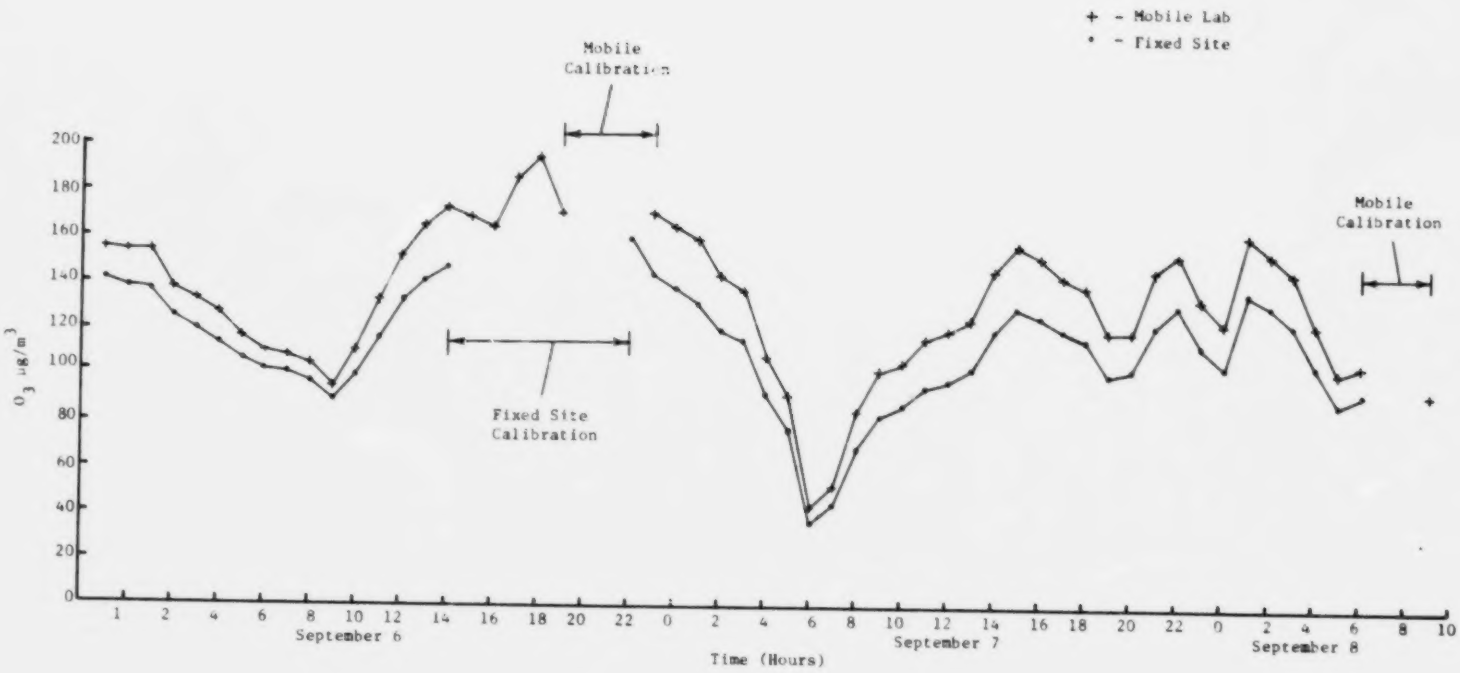


Figure 14. Quality Assurance Program
Kane, Pennsylvania
September 6-8, 1973

4.3 COSHOCTON, OHIO (September 14-19, 1973)

The third site visited during the comparison study was Coshocton, Ohio. The warmup period for the mobile site analyzers began at 1300 on September 14, 1973 and continued until 1400 on September 15, 1973 at which time the calibration of the mobile site analyzers began. Because of a failure of the fixed site ozone analyzer immediately prior to arrival of the mobile van, no comparative data exist between ozone monitors prior to the fixed site biweekly calibration on September 15, 1973. Prior to this calibration, the PM tube of the fixed site analyzer was replaced and the instrument was allowed to warm up for approximately 24 hours. Thus, the only comparison data available are from 1400 on September 18, 1973 to 1100 on September 19, 1973. (See Figure 15.)

Figure 16 indicates that the hourly averages of the fixed site ozone analyzer were less than those indicated by the mobile van. However, on September 19, 1973 around 0800, the ozone concentrations "crossed" and the fixed site ozone hourly averages were greater than those of the mobile van.

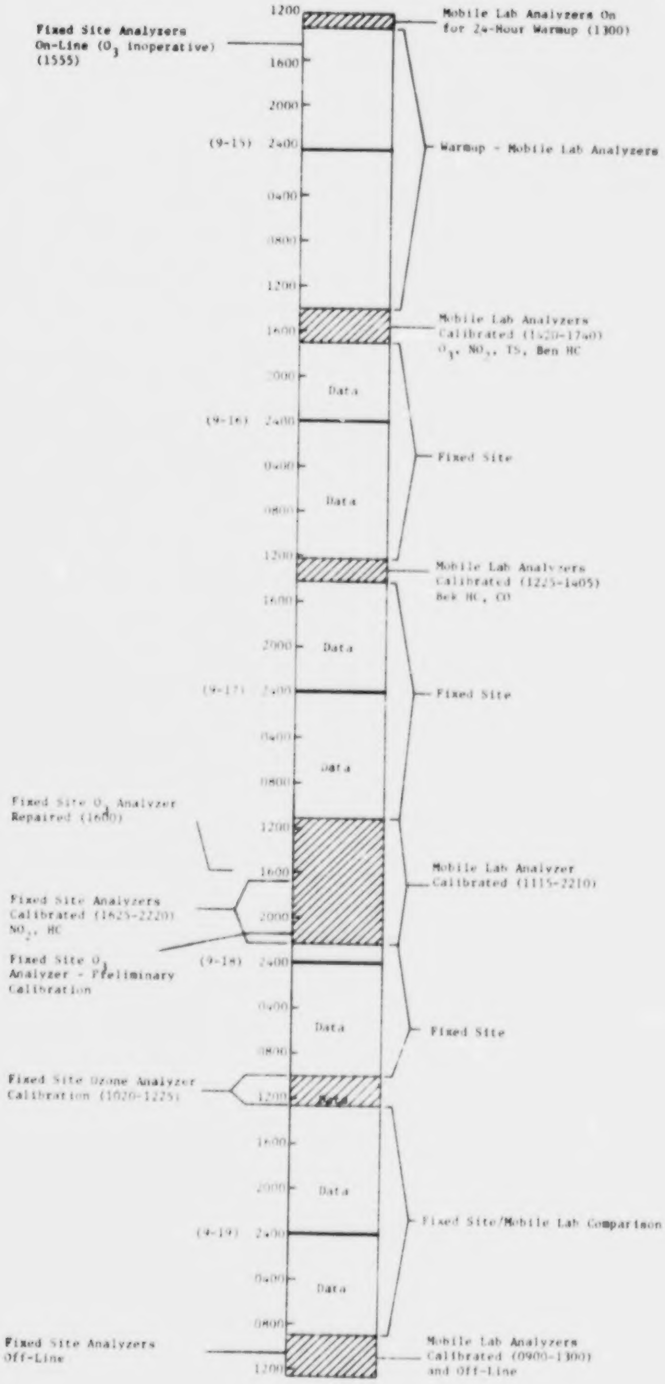

1200
Mobile Lab Analyzers On for 24-Hour Warmup (1300)
Fixed Site Analyzers On-Line (O_3 inoperative) (1555)
1600
2000
(9-15) 2400
Warmup - Mobile Lab Analyzers
0400
0800
1200
1600
Mobile Lab Analyzers Calibrated (1520-1740) O_3, NO_2, TS, Ben HC
2000
Data
(9-16) 2400
Fixed Site
0400
Data
0800
1200
Mobile Lab Analyzers Calibrated (1225-1405) Bek HC, CO
1600
2000
Data
(9-17) 2400
Fixed Site
0400
Data
0800
Fixed Site O_3 Analyzer Repaired (1600)
1200
1600
Mobile Lab Analyzer Calibrated (1115-2210)
Fixed Site Analyzers Calibrated (1625-2220) NO_2, HC
2000
Fixed Site O_3 Analyzer - Preliminary Calibration
(9-18) 2400
0400
Data
Fixed Site
0800
Fixed Site Ozone Analyzer Calibration (1020-1225)
1200
Data
1600
2000
Data
Fixed Site/Mobile Lab Comparison
(9-19) 2400
0400
Data
0800
Fixed Site Analyzers Off-Line
Mobile Lab Analyzers Calibrated (0900-1300) and Off-Line
1200

Figure 15. Fixed Site/Mobile Lab Comparison
September 14-19, 1973
Coshocton, Ohio

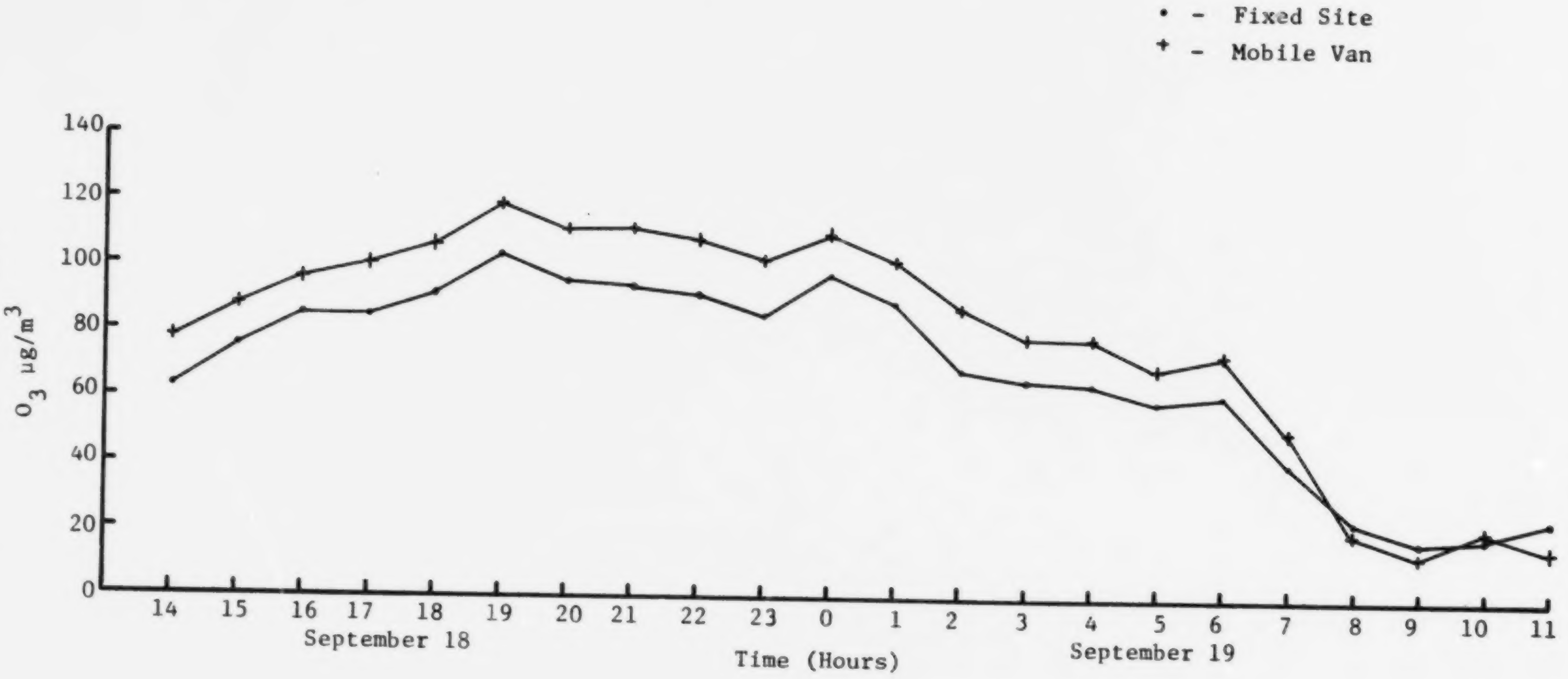


Figure 16. Quality Assurance Program
Coshocton, Ohio
September 18-19, 1973

4.4 GARRETT COUNTY, MARYLAND (September 21-October 3, 1973)

The mobile laboratory arrived at Garrett County, Maryland on September 21, 1973, for an extended period. Part of this time the mobile laboratory (and the fixed site) operated unattended. Figures 17a and 17b present the events for the fourteen day period. Since several calibrations were performed on the mobile van analyzers, there are several possible periods for comparison of the fixed site versus mobile site ozone measurements. The hourly averages for these comparison periods are shown in Figures 18, 19, and 20. Figures 18 and 19 also show the hourly averages from the Westinghouse Pulse-O-Matic data collection system that was located at all the fixed sites and analyzed independently of the mobile laboratory data. The agreement of this data with the fixed site data (as processed by the computer on-board the mobile laboratory) is excellent, thus lending credence to the reliability and accuracy of both the Westinghouse Pulse-O-Matic data system and the processing system used to compute the data from the fixed sites during the rural oxidant study.

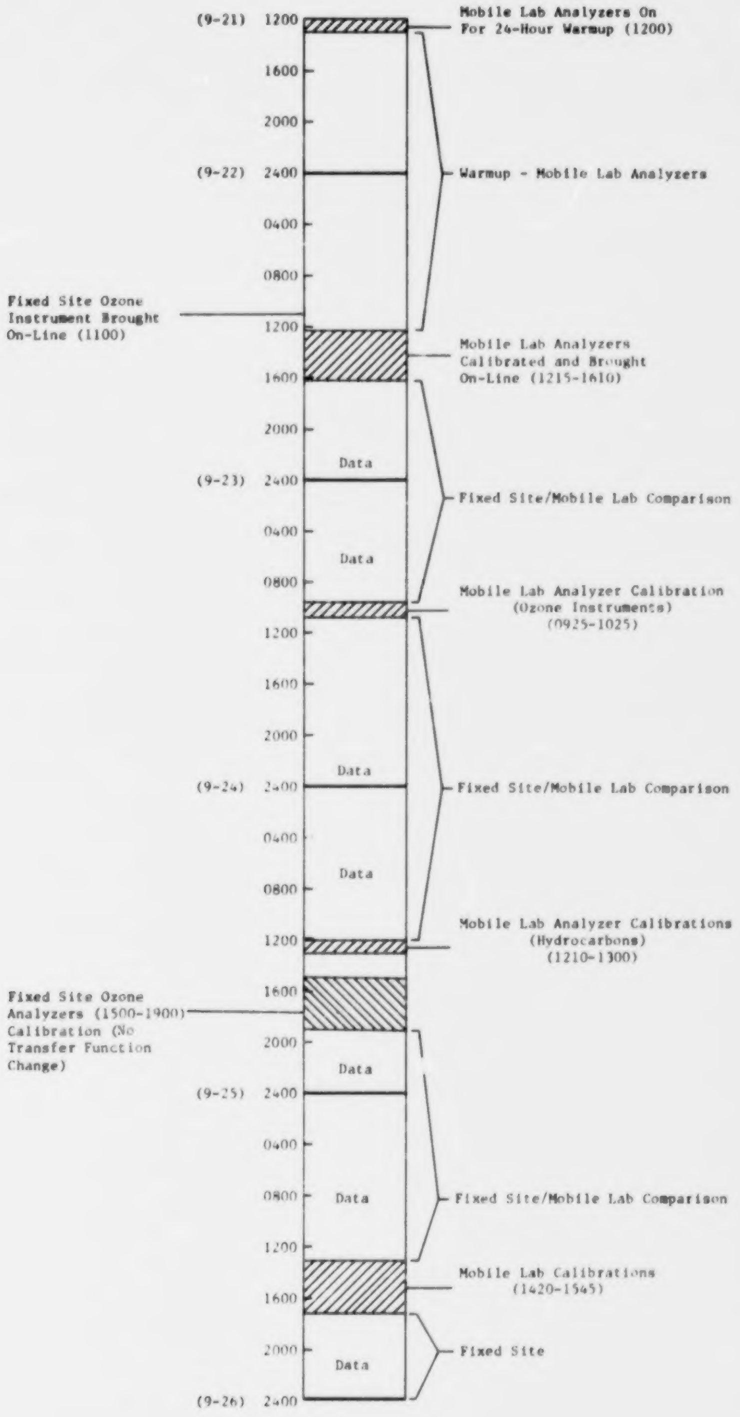

(9-21) 1200
Mobile Lab Analyzers On For 24-Hour Warmup (1200)
1600
2000
(9-22) 2400
Warmup - Mobile Lab Analyzers
0400
0800
Fixed Site Ozone Instrument Brought On-Line (1100)
1200
Mobile Lab Analyzers Calibrated and Brought On-Line (1215-1610)
1600
2000
Data
(9-23) 2400
Fixed Site/Mobile Lab Comparison
0400
Data
0800
Mobile Lab Analyzer Calibration (Ozone Instruments) (0925-1025)
1200
1600
2000
Data
(9-24) 2400
Fixed Site/Mobile Lab Comparison
0400
Data
0800
1200
Mobile Lab Analyzer Calibrations (Hydrocarbons) (1210-1300)
1600
Fixed Site Ozone Analyzers (1500-1900) Calibration (No Transfer Function Change)
2000
Data
(9-25) 2400
0400
0800
Data
Fixed Site/Mobile Lab Comparison
1200
Mobile Lab Calibrations (1420-1545)
1600
2000
Data
Fixed Site
(9-26) 2400

Figure 17a. Fixed Site/Mobile Lab Comparison
September 21-25, 1973
Garrett County, Maryland

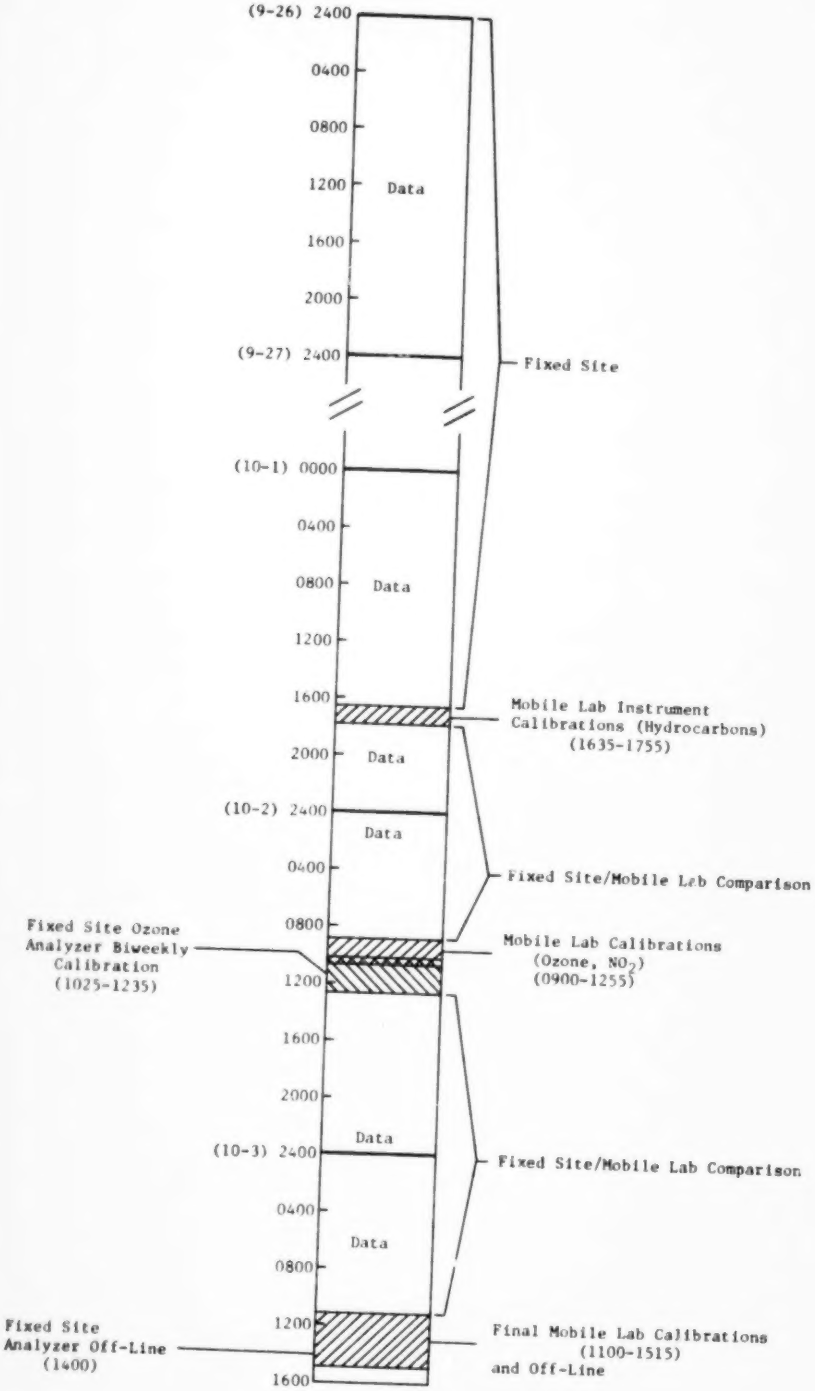

(9-26) 2400
0400
0800
1200
1600
2000
Data
(9-27) 2400
Fixed Site
(10-1) 0000
0400
0800
1200
1600
Data
Mobile Lab Instrument Calibrations (Hydrocarbons) (1635-1755)
2000
Data
(10-2) 2400
Data
0400
Fixed Site/Mobile Lab Comparison
0800
Fixed Site Ozone Analyzer Biweekly Calibration (1025-1235)
Mobile Lab Calibrations (Ozone, NO2) (0900-1255)
1200
1600
2000
Data
(10-3) 2400
Fixed Site/Mobile Lab Comparison
0400
Data
0800
1200
Fixed Site Analyzer Off-Line (1400)
Final Mobile Lab Calibrations (1100-1515) and Off-Line
1600

Figure 17b. Fixed Site/Mobile Lab Comparison
September 26 - October 3, 1973
Garrett County, Maryland

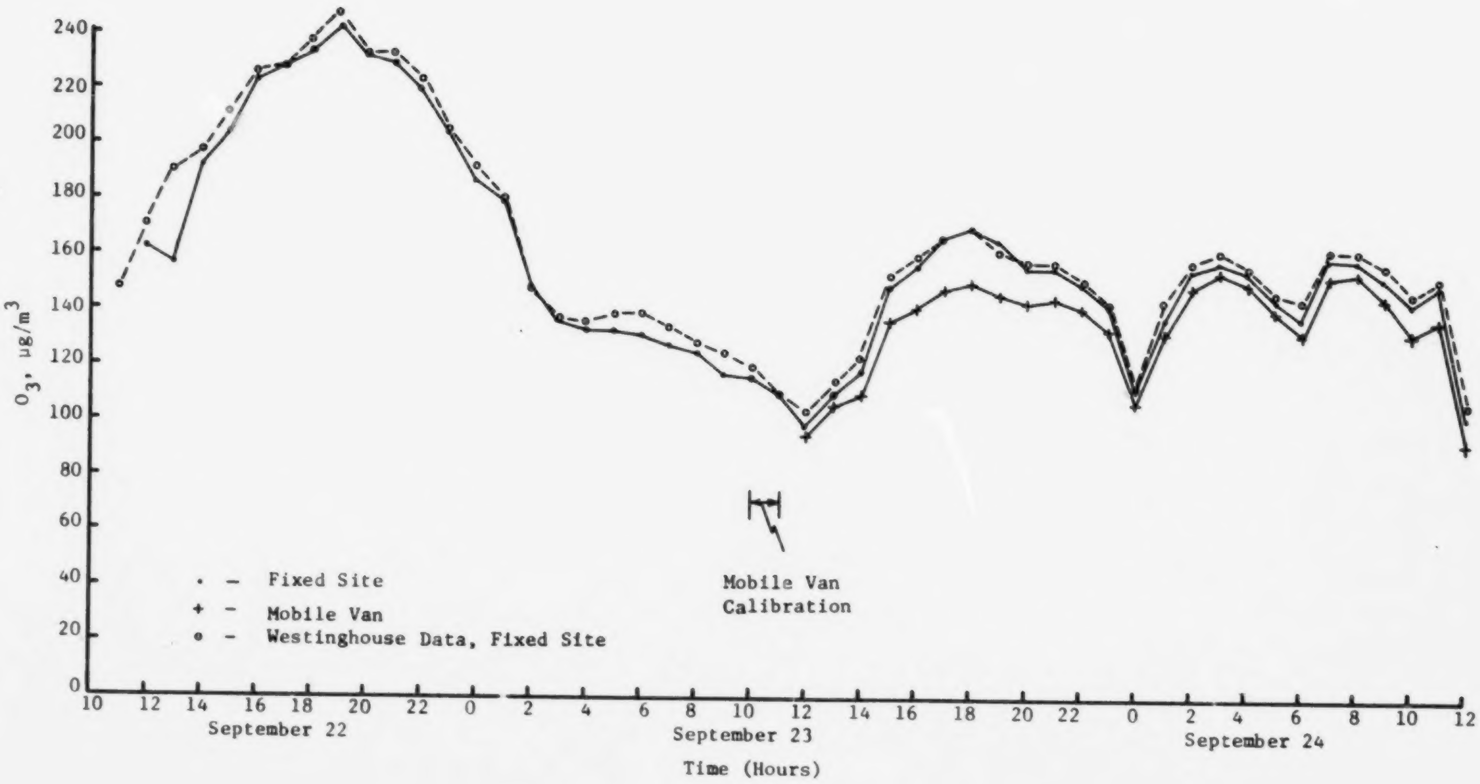


Figure 18. Quality Assurance Program
Garrett County, Maryland
September 22, 23, 24, 1973

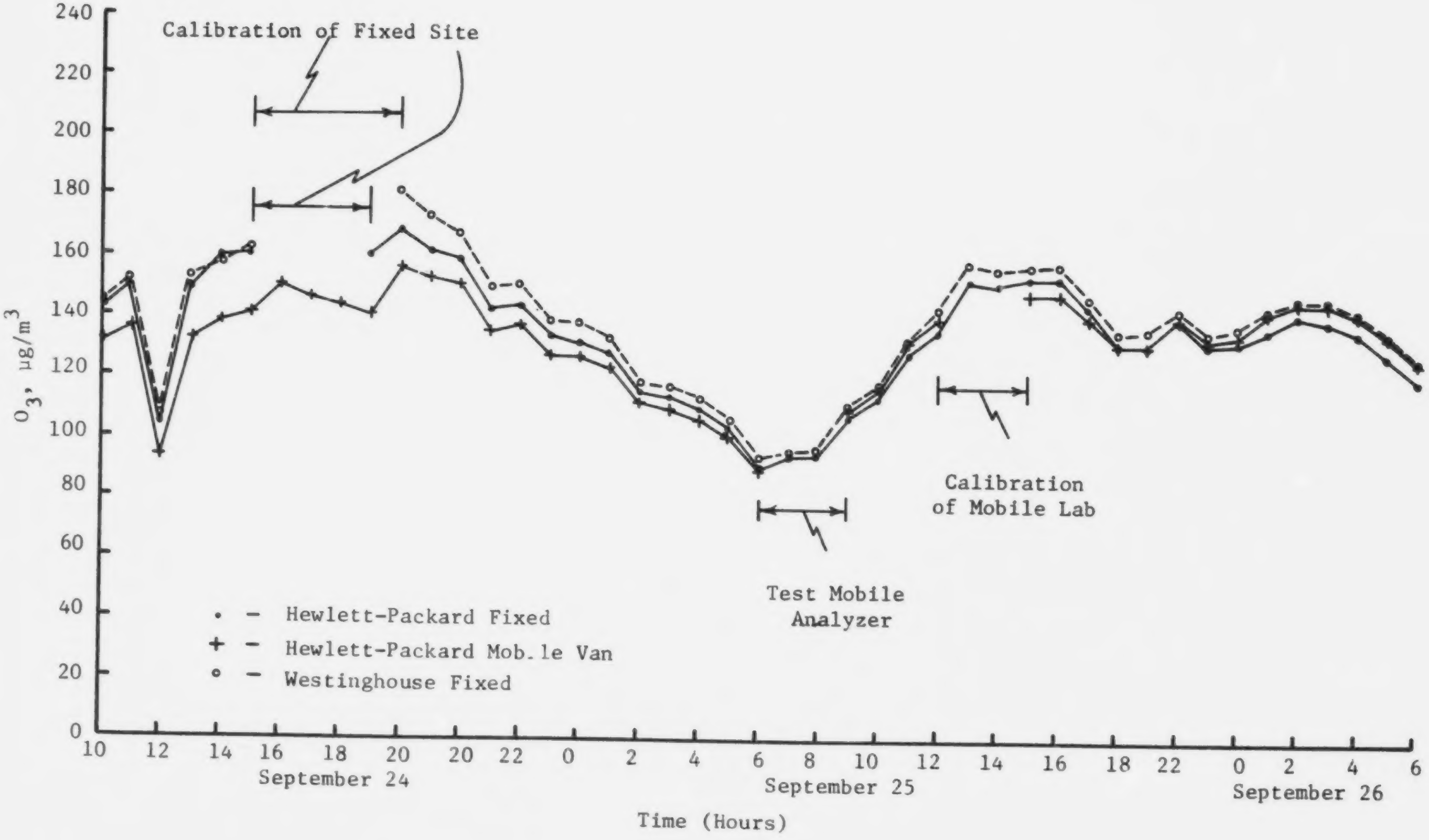


Figure 19. Quality Assurance Program
Garrett County, Maryland
September 24, 25, 26, 1973

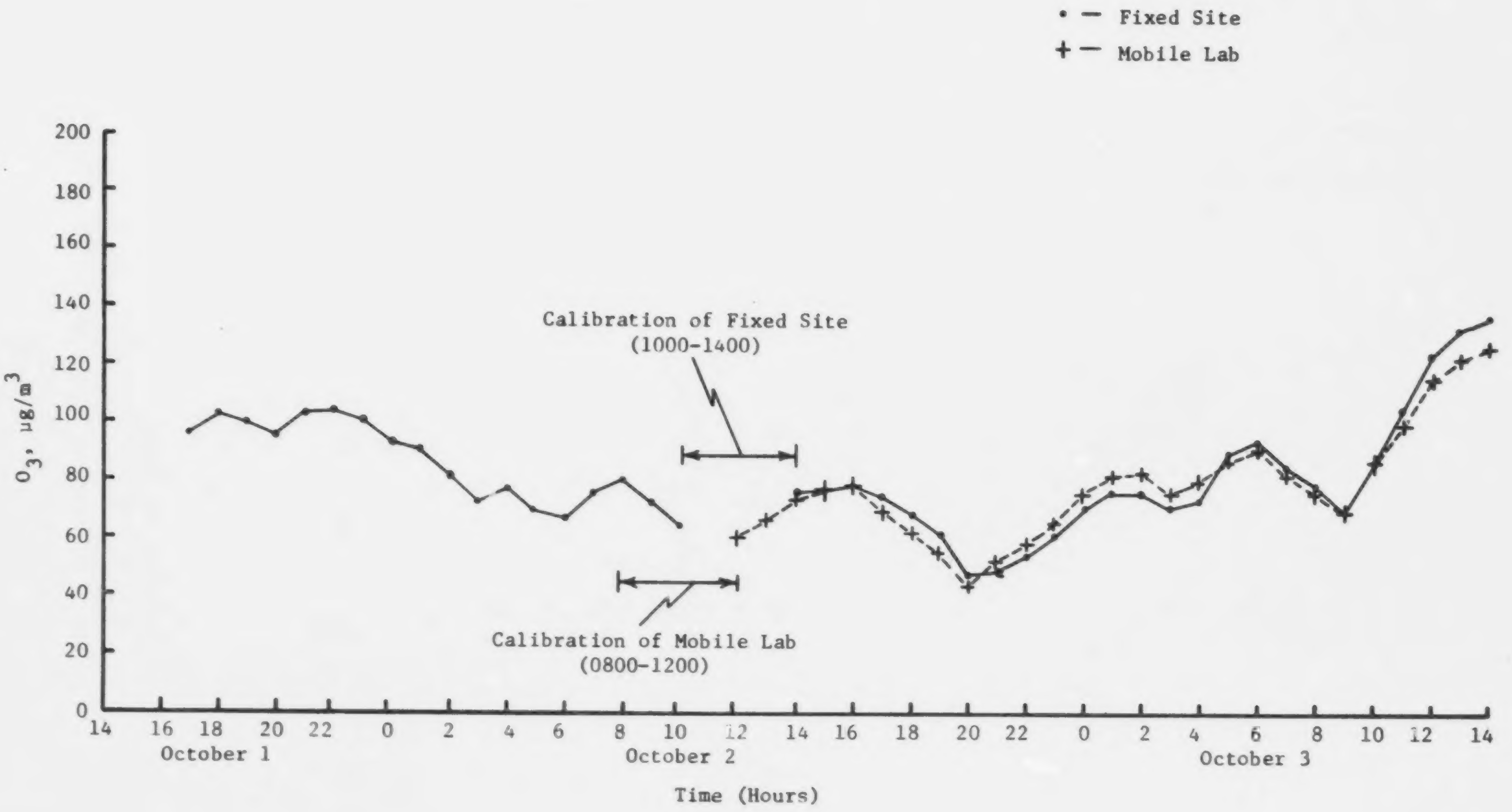


Figure 20. Quality Assurance Program
Garrett County, Maryland
October, 1, 2, 3, 1973

4.5 LEWISBURG, WEST VIRGINIA (October 4-8, 1973)

A second comparison period was initiated at Lewisburg, West Virginia during the period October 4-8, 1973, mainly to obtain additional hydrocarbon data. The mobile and fixed analyzers were calibrated at about the same time on October 5; thus, the comparison period for ozone is restricted to data after calibration. The study ended on October 8, 1973. (See Figure 21.)

Figure 22 shows that excellent agreement was obtained between the mobile and fixed ozone analyzers for the two-day period.

Comparison of total hydrocarbon and nonmethane hydrocarbon measurements from the Bendix 8201 and the Beckman 6800 analyzers indicated an elevated response of the Bendix analyzer to ambient concentrations of total hydrocarbons. Moisture was suspected as the interferent and subsequent tests at Bendix confirmed the suspicion. This conclusion and the confirming evidence uncovered at Lewisburg and other sites were responsible for invalidating all hydrocarbon data collected at the four sites during the rural oxidant study.

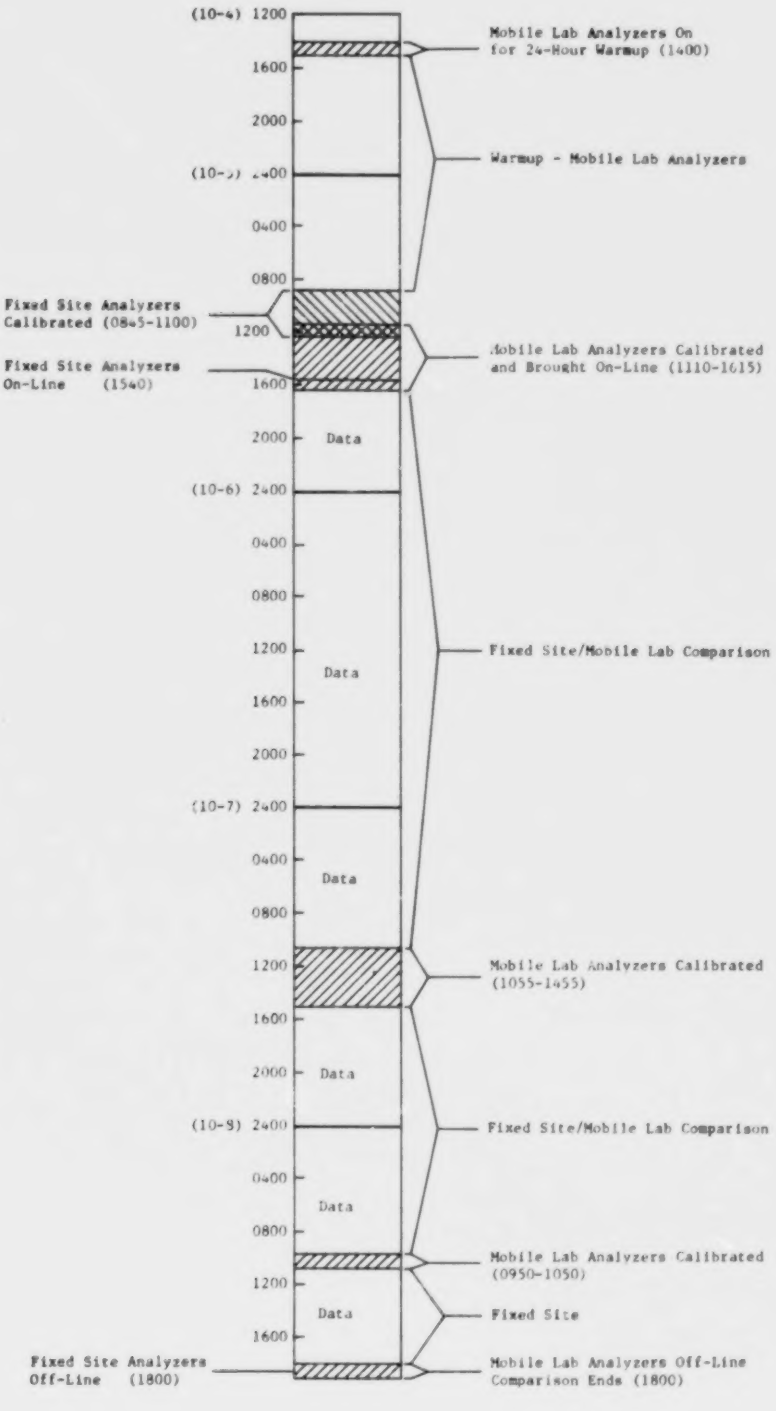

(10-4) 1200
Mobile Lab Analyzers On for 24-Hour Warmup (1400)
1600
2000
Warmup - Mobile Lab Analyzers
(10-5) 2400
0400
0800
Fixed Site Analyzers Calibrated (0845-1100)
1200
Mobile Lab Analyzers Calibrated and Brought On-Line (1110-1615)
Fixed Site Analyzers On-Line (1540)
1600
2000
Data
(10-6) 2400
0400
0800
1200
Data
Fixed Site/Mobile Lab Comparison
1600
2000
(10-7) 2400
0400
Data
0800
1200
Mobile Lab Analyzers Calibrated (1055-1455)
1600
2000
Data
(10-8) 2400
Fixed Site/Mobile Lab Comparison
0400
Data
0800
Mobile Lab Analyzers Calibrated (0950-1050)
1200
Data
Fixed Site
1600
Fixed Site Analyzers Off-Line (1800)
Mobile Lab Analyzers Off-Line Comparison Ends (1800)

Figure 21. Fixed Site/Mobile Lab Comparison
October 4-8, 1973
Lewisburg, W. Va.

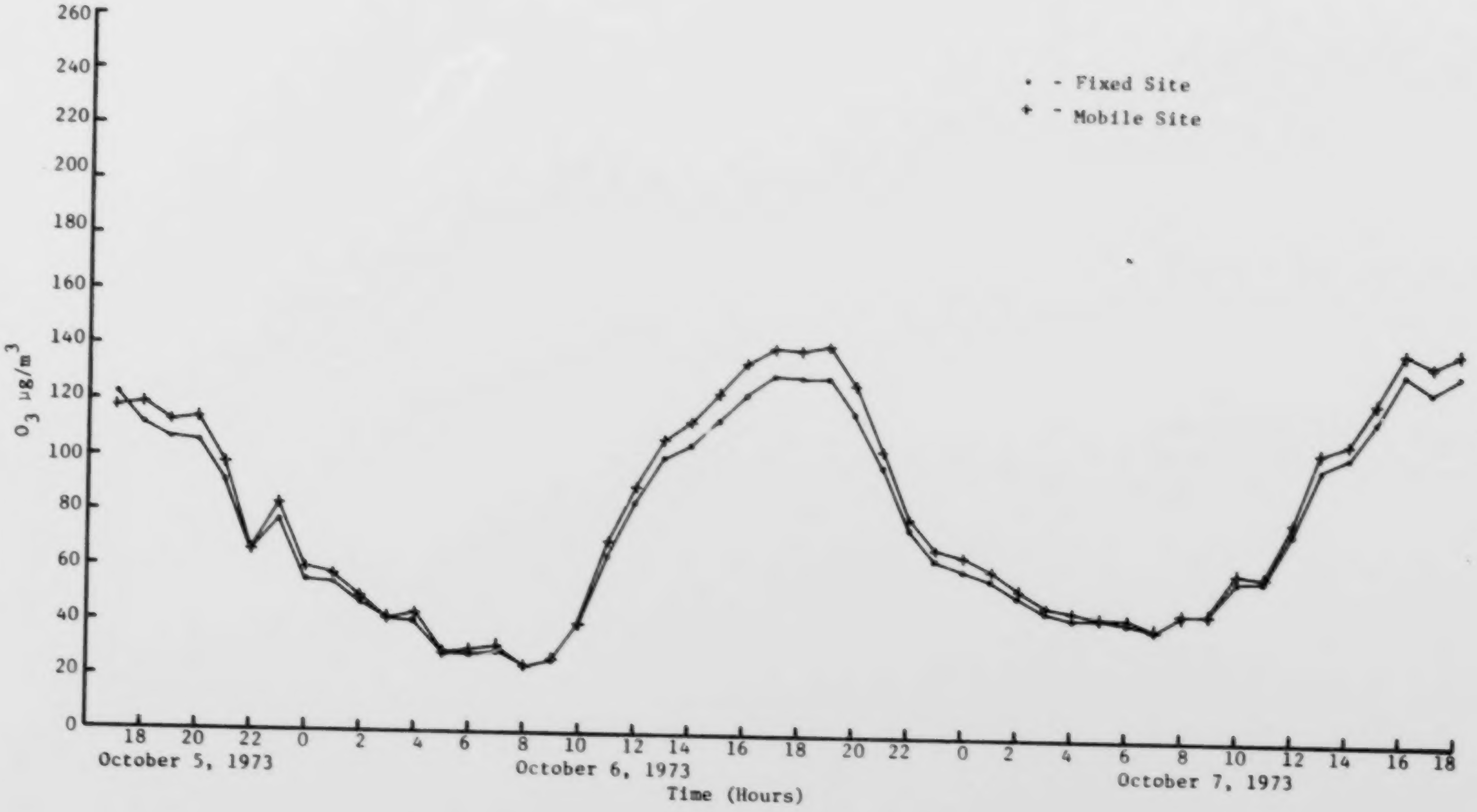


Figure 22. Quality Assurance Program
Lewisburg, W. Va.
October 5, 6, 7, 1973

5.0 STATISTICAL ANALYSIS

Selected data obtained during the quality assurance program at each site (Appendix B) were analyzed to determine the comparability and relationships between the fixed and mobile site ozone measurements. The results of these analyses are summarized in Table 4 and include the correlation coefficient, mean, range, standard deviation about the mean, ratio of fixed to mobile means, estimated bias, percent relative bias, and the number of observation periods both prior to and after the calibration of the fixed and/or mobile site analyzers.

In general, there were two comparison periods as shown in Figure 5. The first comparison period was for approximately 16 hours and occurred after dynamic calibration of the mobile site ozone analyzer and before the regular biweekly multipoint calibration of the fixed site ozone analyzer. The second period of comparison was approximately 24 hours and occurred after the fixed site calibration. In some cases, there were other comparison periods following additional calibrations of the mobile site analyzer.

Code numerals were assigned to the mobile (M) and fixed (F) site ozone analyzers in Table 4 to denote different comparison periods and are as follows:

M-1	Comparison period following first calibration of mobile site analyzer.
M-2	Comparison period following second calibration of mobile site analyzer.
M-3	Comparison period following third calibration of mobile site analyzer.
F-1	Comparison period preceding calibration of fixed site analyzer.
F-2	Comparison period following calibration of fixed site analyzer.

Table 4. PAIRED COMPARISONS ON OZONE MOBILE VAN VERSUS FIXED SITE

SITE	COMPARISON PERIOD MOBILE	FIXED	CORRELATION (M, F)	MEAN* MOBILE	FIXED	RANGE* MOBILE	FIXED	STANDARD DEV.* MOBILE	FIXED	EST.* BIAS	RATIO OF MEANS F/M	RELATIVE BIAS (PERCENT)	N
Lewisburg August 28-31, 1973	1	1	0.9871	78.3	96.2	27-165	36-207	31.4	39.0	+17.9	1.23	23	53
	2	2	0.9969	41.8	33.7	28-69	19-63	10.8	11.3	-8.1	0.81	-19	42
	3	2	0.9916	117.6	106.2	37-239	31-234	64.8	62.1	-11.5	0.90	-10	92
Kane September 6-8, 1973	1	1	0.9936	134.2	120.7	93-178	89-151	24.5	18.8	-13.5	0.90	-10	66
	2	2	0.9967	127.4	107.4	28-181	24-158	31.2	26.5	-20.0	0.84	-16	129
Coshocton September 18-19, 1973	2	2	0.9694	78.8	68.4	13-124	15-110	33.4	27.6	-10.4	0.87	-13	75
Garrett Co. September 22-October 3, 1973	1	1	0.9659	135.0	145.2	80.156	88-174	18.3	20.8	+10.2	1.08	8	114
	2	2	0.9834	125.8	129.3	86-160	88-174	19.2	22.0	+3.5	1.03	3	68
	3	2	0.9780	133.4	135.3	96-183	91-196	19.7	25.3	+2.0	1.01	1	248
	4	2	0.9805	80.0	81.2	39-135	42-144	20.6	22.8	+1.2	1.02	2	101
Lewisburg October 6-8, 1973	2	2	0.9943	74.8	71.6	22-151	23-157	37.1	33.8	-3.2	0.96	-4	281

*Units = $\mu g/m^3$

Estimated bias = Σ(Fixed - Mobile) /N

N = no. of 15 minute time periods

Ratio F/M = Ratio of the means

Relative bias (percent) = $\left(\frac{\text{Fixed Mean}}{\text{Mobile Mean}}\right) - 1 \times 100$

Each observation period used in the comparison consisted of a pair of fifteen minute ozone averages, one each from the fixed and mobile sites. Four comparison periods were available for Garrett County, three for Lewisburg, and two for Kane. Due to the failure of the fixed ozone analyzer at Coshocton, immediately prior to the arrival of the mobile laboratory, the only comparison period for that site was after repair and calibration of the fixed site analyzer and calibration of the mobile site analyzer.

Brief summations of the comparison results between measurements of ozone from the fixed and the mobile sites are presented in the following paragraphs. Each summary pertains to the time frame indicated in Table 4 for each site. Certain qualifications should be restated prior to presentation and interpretation of the comparison results. These are as follows:

1) Two independent monitoring systems sampling from a common sampling point were used to generate each pair of data points.

2) Identical brand-name ozone analyzers were used where possible.

3) Independent test atmosphere generating systems were used to provide calibration concentrations to the respective analyzers in the fixed and mobile sites.

4) Each ozone calibration concentration was verified by manual iodometric analysis.

5) Individual differences were minimized and continuity was maintained throughout the quality assurance program by using qualified personnel to calibrate the ozone analyzers in the respective stations.

A. Lewisburg, West Virginia (August 28-31, 1973)

The data presented in Table 4 show excellent correlation between the fixed and mobile site ozone measurements both prior to and after the fixed site calibration. Correlation coefficients ranged from 0.98 to >0.99. The ratio of the fixed to mobile mean values, however, was 23 percent higher prior to the calibration of the fixed site analyzer. A possible reason for this estimated bias (18 $\mu g/m^3$) could be span drift of the fixed site analyzer since the previous biweekly calibration. Upon calibration of the fixed site analyzer, there was a reversal in the mean ratio; however, there was also a marked reduction in the range of the ozone measurements. Explanations for the change in bias immediately after calibration of the fixed site analyzer could be related to differences in calibration systems and differences in techniques of individuals performing the manual iodometric analyses during calibration. Also, analyzers in the mobile laboratory operated on regulated line voltage, whereas the fixed site was not equipped with a line voltage regulator. After a second calibration of the mobile site analyzer, the ratio of the means was 0.90.

B. Kane, Pennsylvania (September 6-8, 1973)

Excellent correlation was obtained at Kane between the fixed and mobile site ozone measurements both prior to and after the calibration period. On the average, the mobile site analyzer indicated 10 to 16 percent higher ozone values than the fixed site analyzer with biases of -13 to -20 $\mu g/m^3$ for the respective periods.

C. Coshocton, Ohio (September 18-19, 1973)

The correlation coefficient for the one comparison period at Coshocton was 0.97, and the ratio of the mean was 0.87. An average bias of -10 $\mu g/m^3$ was exhibited between the two analyzers.

D. Garrett County, Maryland (September 22 - October 3, 1973)

The data presented in Table 4 show excellent correlation between the fixed and mobile site analyzers with the correlation coefficient ranging from 0.97 to 0.98. The ratio of means did not change significantly after calibration of either the fixed or mobile site analyzers, and the average bias for the entire period was less than 5 percent.

E. Lewisburg, West Virginia (October 6-8, 1973)

The return visit to Lewisburg coincided with the regular biweekly calibration of the fixed station analyzers. Excellent correlation was obtained between the two measurements with the mobile site analyzer reading approximately 4 percent higher on the average. The difference between the fixed and mobile site analyzer measurements was much less than during the first comparison period (see A).

6.0 SUMMARY AND CONCLUSIONS

The purpose of this program was to provide some measure of the comparability of the data being generated at four fixed stations during the rural oxidant program conducted by RTI during the summer of 1973. The objective was accomplished by comparison of measurements obtained by instrumentation housed in a mobile laboratory with those obtained from the four fixed stations under routine operating conditions, both prior to and after calibration of the fixed site analyzers. The RTI Environmental Monitoring Laboratory, equipped with a full complement of air quality analyzers, calibration systems, data acquisition system, and on-line computer capable of processing data in real-time, was transported to each of the respective sites and was set up adjacent to the fixed station; comparative data were obtained for the measurement parameters from both the fixed and mobile site analyzers. The duration of the comparison period varied somewhat due to the operational status of the analyzers in the respective stations. In general, the time frame presented in Figure 5 (Section 3.1) was adhered to. Air sampling inlets for both stations were located at a common point, so that identical samples of ambient air were provided to both sets of analyzers. Data were processed in real time for both sets of analyzers (i.e., fixed and mobile), so that instrument outputs in $\mu g/m^3$ could be examined immediately. This feature was necessary for preliminary comparison of data and check on the monitoring system. Following the comparison periods at each site, the Environmental Monitoring Laboratory was returned to Research Triangle Institute and the data subjected to statistical analysis.

Due to the constraints previously mentioned regarding extremely low NO_2 values and the invalidation of all hydrocarbon data from the fixed sites, the only pollutant considered for the comparison evaluation was ozone. Statistical analysis included computation of correlation coefficients, means, ranges, standard deviations about the mean, ratio of fixed to mobile means, and estimated bias during each comparison period, both prior to and after calibration of the fixed and/or mobile site analyzers.

Excellent correlation was obtained at each site between the fixed and mobile site ozone measurements both prior to and after each calibration period. Correlation coefficients ranged from 0.97 to >0.99 within a site and comparison period. Level differences were observed between measurements from the fixed and mobile site analyzers at each site as indicated by the estimated bias of the measurements. The average estimated bias ranged from 18 to -20 $\mu g/m^3$ over the entire comparability program (i.e., over the 11 comparison periods at the four stations). The greatest relative bias existed at Lewisburg (23%) prior to the calibration of the fixed site analyzer, and the least relative bias was at Garrett County (8%). After calibration the relative bias at Lewisburg decreased considerably, indicating that the bias in the measurement was related to span drift of the fixed site analyzer since the previous calibration, to a faulty calibration, to variation in the manual iodometric analyses used to determine the ozone calibration concentrations and/or to a combination of all three. With respect to the Kane and Coshocton sites and the Lewisburg site after calibration, a consistent negative relative bias of 10 to 16 percent was observed. The positive relative bias at Garrett County and Lewisburg

(2nd visit) between the fixed and mobile site measurements averaged approximately 3 percent. In the above discussion, the mobile site data were used as a measure of the absolute concentration of ozone. It is recognized that this assumption is not entirely correct; however, these data should be more precise and accurate than the fixed site data because they were essentially obtained under controlled laboratory conditions.

Pertinent observations that can be drawn from the data are as follows:

(1) The high correlation between the fixed and mobile site ozone measurements (i.e., 0.97 to >0.99) confirms that the ozone analyzers at each site were measuring the same variable--but not necessarily generating the same numbers.

(2) Level differences (bias) did exist at each site between the fixed and mobile site ozone measurements. The estimated bias over all sites and comparison periods ranged from 18 to -20 $\mu g/m^3$ [$(\Sigma$ Fixed - Mobile$)/N$].

(3) The average relative bias over all sites and for all comparison periods was less than 10 percent. Excursions from this limit did occur; this information was used to identify problem areas and take corrective action.

(4) Bias between the fixed and mobile site ozone measurements generally decreased immediately after calibration and/or recalibration of the fixed or mobile site analyzers.

Bias between the fixed and mobile site measurements could be due to many factors, such as instrument performance (drift, response, etc.), operator variables, calibration techniques and frequency, environmental factors (temperature and line voltage variation), and concentration level of ozone.

The overriding consideration for this program was to provide a means for determining the comparability and interrelatability of data obtained from four widely dispersed fixed air monitoring systems. This was accomplished by systematic comparison to data from the mobile air monitoring facility, which was considered to be more reliable due to better environmental control, sophistication of equipment (i.e., calibration and data acquisition systems, data processing facilities) and experience of personnel. This approach is novel in that it provides a mechanism for validation of the operation of the entire monitoring facility, not just the analyzer itself. This includes the air sampling system, the performance of the air quality analyzer, the data recording system, and the system utilized to process and output the data.

Recommendations for future work involving field measurement programs include the use of a mobile air monitoring facility as a quality assurance tool to verify and validate data from network air monitoring stations. Proper use of a mobile facility to determine the bias of individual stations would allow for comparison between pollutant levels in different parts of the country with better confidence. Increasing the frequency of the comparison periods for field sites to the mobile air monitoring facility would give an estimate of the precision of the estimated bias.

APPENDIX A

CALIBRATION SYSTEMS/PROCEDURES

1.0 CALIBRATION SYSTEMS

1.1 Ozone

A dynamic calibration system as described by Hodgeson et al.[1] and published with the National Primary and Secondary Ambient Air Quality Standards[2] was used to calibrate the ozone instrumentation evaluated during this study. Briefly, the ozone source consists of an 8-inch ultraviolet mercury lamp which irradiates a 5/8-inch quartz tube through which clean (compressed) air flows at 5 liter/minute. Ozone concentrations from 0 to approximately 1 ppm (1960 $\mu g/m^3$) can be generated by moving the shield and exposing various lengths of the lamp. Although the UV O_3 generator has been shown to be quite stable and reproducible,[1,3] the neutral-buffered potassium iodide technique was used as the reference method.[2] A permanent calibration setup consisting of a zero air source, calibrated rotameter, UV generator, and a glass manifold was installed in the laboratory facility and calibrated by the manual neutral-buffered potassium iodide procedure periodically during the study. A diagram of the calibration system is shown in Figure A-1. An identical but portable system was used to calibrate the ozone analyzers in the fixed stations during this study. All calibration concentrations were verified by manual iodometric analysis.

1.2 Nitric Oxide/Nitrogen Dioxide

Due to problems associated with long-term use of NO_2 permeation tubes and the need to routinely determine the efficiency of the carbon, stainless steel, or molybdenum converters (which reduce NO_2 to NO), an alternative procedure (gas phase titration) was used for routine dynamic calibration of the chemiluminescent $NO\text{-}NO_x\text{-}NO_2$ analyzers. The gas phase titration technique is based upon application of the rapid gas phase reaction between NO and O_3 to produce a stoichiometric quantity of NO_2[4,5]

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu \ .$$

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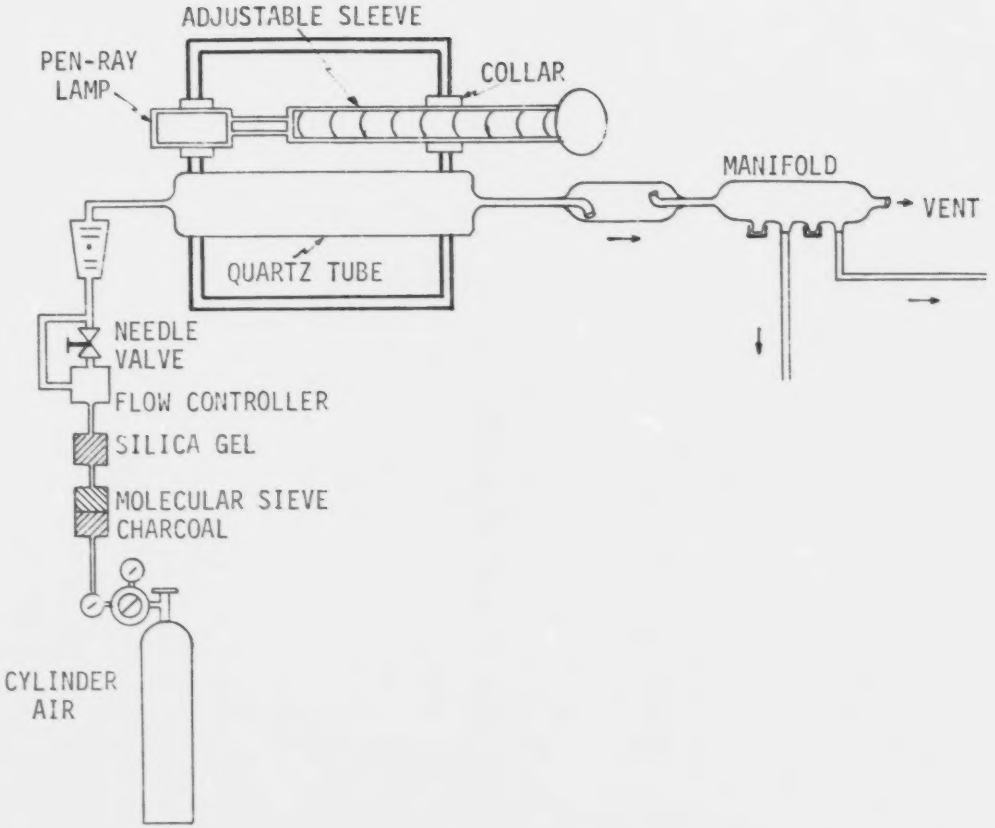
ADJUSTABLE SLEEVE
PEN-RAY LAMP
COLLAR
MANIFOLD
VENT
QUARTZ TUBE
NEEDLE VALVE
FLOW CONTROLLER
SILICA GEL
MOLECULAR SIEVE
CHARCOAL
CYLINDER AIR

Figure A-1. Ozone Analyzer Calibration System

Nitric oxide from a cylinder of NO in N_2 (50 ppm) is diluted with a constant flow of clean air to provide 1.0 ppm and used to calibrate the NO and NO_x cycles of the chemiluminescent $NO-NO_x-NO_2$ analyzer. By incorporation of a calibrated ozone generator in the calibration apparatus upstream from the point of NO addition, precise NO_2 concentrations can be generated by oxidation of NO to NO_2 with O_3. A schematic diagram showing the component parts of the calibration system is presented in Figure A-2. As long as a slight excess of NO is present, the concentration of O_3 added is equivalent to the concentration of NO consumed and is equivalent to the concentration of NO_2 generated.

A general description of this calibration scheme is presented in the following paragraphs. Primary calibration of the NO concentration in the pressurized cylinder containing nitrogen as a diluent is accomplished by titration of an NO concentration of 1.0 ppm produced by dilution with successive concentrations of ozone (0-0.8 ppm) generated by an ozone generator which has been referenced to the neutral-buffered KI procedure.[6] The resultant NO detector outputs after stabilization at each titration point (i.e., 0.0,0.1,0.2, --- 0.8 ppm ozone added) are plotted in ppm on coordinate graph paper (y-axis) versus O_3 concentrations added, ppm (x-axis). A straight line is drawn through the linear portion of the iteration curve and extrapolated to the x-axis. The concentration at the x-axis intercept, C_0', is the O_3 concentration equivalent to the initial diluted NO concentration. An example of a typical gas phase titration curve is presented in Figure A-3. The concentration of NO in the cylinder can then be determined as follows:

$$C_{NO} = \frac{F_0 \times C_0'}{F_{NO}}$$

where

C_{NO} = cylinder NO concentration, ppm,
F_{NO} = measured NO flow, cc/min,
C_0' = equivalence point O_3 concentration, ppm,
F_0 = total clean air flow, cc/min.

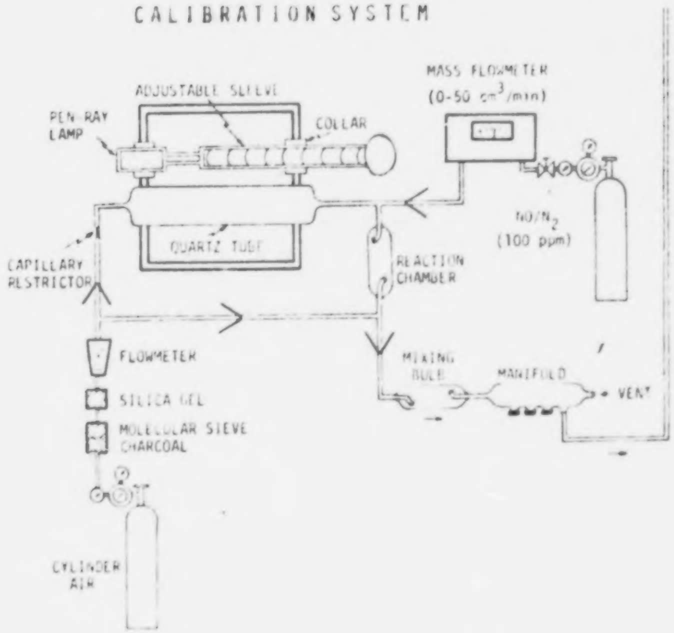
CALIBRATION SYSTEM
MASS FLOWMETER
(0-50 cm^3/min)
ADJUSTABLE SLEEVE
PEN-RAY LAMP
COLLAR
NO/N_2
(100 ppm)
QUARTZ TUBE
CAPILLARY RESTRICTOR
REACTION CHAMBER
FLOWMETER
MIXING BULB
MANIFOLD
VENT
SILICA GEL
MOLECULAR SIEVE CHARCOAL
CYLINDER AIR

Figure A-2. Gas phase titration system

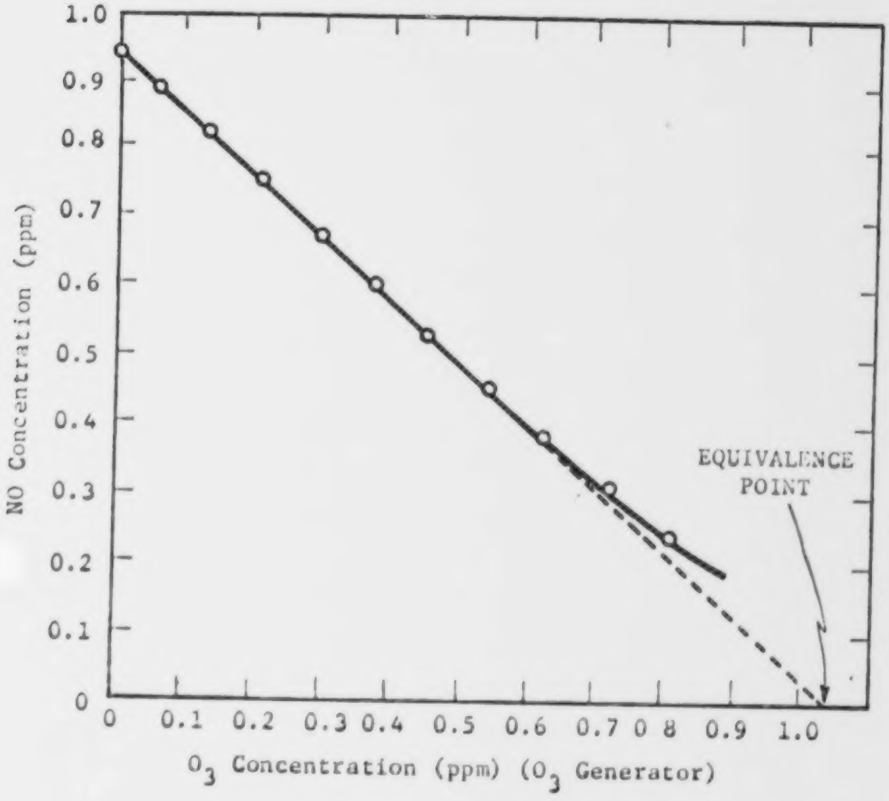

Figure A-3. Gas-phase titration of NO with O_3.

Once the NO concentration in the cylinder has been determined, this cylinder can be used over its lifetime to provide a working standard for routine calibration[6]; however, to assure validity of data, the NO concentration should be verified at one-month intervals.

During routine calibration, the NO and NO_x channels of the chemiluminescent NO-NO_x-NO_2 analyzers were calibrated by dynamic flow dilution of the NO in nitrogen cylinder gas. To calibrate the NO_2 output channel and to determine the converter efficiency (i.e., efficiency of reduction of NO_2 to NO), a constant concentration of 0.5 or 1.0 ppm of NO is produced in the flow system. Ozone is then added in increments from the variable O_3 source. The incremental decrease of the NO measurement is then equivalent to the concentration of NO_2 produced by the gas phase titration reaction. In this scheme the calibrated O_3 source becomes a calibrated NO_2 source when NO is present in excess.

6.1.3. Hydrocarbons

Calibration of hydrocarbon instruments was accomplished utilizing standard calibration gases certified by the supplier. For this study cylinders of methane in air were obtained from Scott Research Laboratories. Several concentrations ranging from 0 to 10 ppm of CH_4 were used for calibration purposes. In the absence of acceptable cylinders of zero air (i.e., CH_4 < 0.01 ppm) an alternative procedure utilizing electronic zeroing was used in lieu of dynamic zero. The following concentrations of methane in air were used to calibrate hydrocarbon analyzers:

Supplier	Cylinder #	Certification by Manufacturer (± 2%)
Scott Research Laboratories	A	1.2 ppm
	B	4.2 ppm
	C	7.5 ppm

2.0 GENERAL CALIBRATION PROCEDURE

A general procedure applicable to the dynamic calibration of any analyzer was utilized in this investigation. Procedures and features developed during the previous studies[7, 8, 9] such as mode switch inputs describing instrument operational status and automatic entry of calibration data on magnetic tape were combined with on-line computer computation of transfer equations by linear regression analysis of calibration data and processing of air quality data in quasi real-time.

The basic step-wise procedure employed for dynamic calibration of all air quality analyzers was as follows:

(1) Verify operational status of each analyzer prior to beginning calibration.

(2) Connect instrument inlet line or instrument calibration inlet line, as the case may be, to the manifold of the calibration apparatus or for hydrocarbon instruments, directly to cylinders containing calibration gas.

(3) Allow instrument to sample zero air (i.e., air minus the pollutant of concern) for a period of time sufficient to establish a valid zero output. Indicate the proper manual entry status code for zero and average the instrument output for zero input concentration for at least 15 minutes.

(4) Introduce a pollutant calibration concentration equal to approximately 80 percent of the operating range and adjust the span of instrument as required upon initial setup of the instrument. This adjustment is normally required only upon initial setup of an instrument or if excessive span drift occurred during the evaluation period. Minor adjustments in the span of each instrument can be performed by the on-line computer more easily than by manual adjustment of the span control knob, except for cases where drastic changes in span occurred. Omit Step (4) except on initial setup of analyzer.

(5) Introduce successive pollutant calibration concentrations of 10, 20, 40, 60, and 80 percent of the operating range of the instrument being calibrated. Allow sufficient time to establish a valid instrument output for each calibration concentration, and average the instrument output for that input calibration concentration for at least 15 minutes. Indicate the proper manual entry status codes for multi-point calibration and proceed to the next higher calibration concentration and repeat the sequence of events for multi-point calibration.

(5) Return the instrument inlet line to the ambient air sampling manifold and compute the transfer equation, which relates pollutant concentration input to instrument voltage output, for each instrument. This function was automatically computed at the end of each calibration by the on-line mini-computer employed during this instrument evaluation program.

The frequency of calibration performed during this investigation varied from daily (mobile site) to biweekly (fixed sites). All calibration concentrations were verified by manual iodometric analyses (neutral-buffered KI procedure).

3.0 DETAILED CALIBRATION PROCEDURES

3.1 CALIBRATION PROCEDURE FOR BENDIX OZONE ANALYZER

1) Set up ozone analyzer according to manufacturer's instructions.

2) Allow sufficient time for warmup stabilization period.

3) Introduce zero air and establish zero baseline and record mV outputs.

4) Introduce an ozone concentration equal to approximately 80 percent of the operating range. Adjust span control as required and record value.

5) Introduce ozone concentrations of 10, 20, 40, 60 percent of the operating range and record respective mV outputs without additional adjustments. Determine the ozone concentration for each calibration point in $\mu g/m^3$ using the neutral-buffered KI method as described in the April 30, 1971 Edition of the Federal Register.

6) Establish a line of best fit using method of least squares for the calibration curve.

3.2 CALIBRATION PROCEDURE FOR BENDIX NO-NO_x-NO_2 ANALYZER

1. Turn on ozone generator and Hastings Mass Flowmeter and allow them to warm up for approximately 15-20 minutes.
2. Connect instrument inlet line to manifold of calibration apparatus. Connect compressed air cylinder to calibration apparatus and allow zero air (air filtered through charcoal) to flow through system. Connect NO/N_2 gas regulator to cylinder and evacuate with pump to prevent the formation of NO_2 in the regulator.
3. Allow analyzer to sample zero air for 5-10 minutes. Average zero output for NO, NO_x, and NO_2 channels for at least 5 cycles (i.e., 5 minutes). If instrument zero deviates from zero by more than ±10 millivolts, readjust to zero. Indicate proper entry codes for zero and/or zero adjust on magnetic tape.
4. Prepare 0.1 ppm NO concentration by appropriate dilution by metering sufficient NO (5 cc/min) in nitrogen into 5 liter/min diluent stream. Allow 5 minutes for system to equilibrate and then average first calibration point until instrument output has equilibrated. Enter proper codes on magnetic tape using mode switches. Enter calibration concentration on magnetic tape using 10-turn potentiometer. Both NO and NO_x channels are calibrated simultaneously.
5. Proceed to next calibration concentration and repeat step #4 (i.e., for 0.1, 0.2,0.4,0.5 ppm NO, etc.).

6. After completing multipoint calibration with NO, generate NO_2 concentrations as described in the previous discussion. Enter proper codes and calibration concentrations on magnetic tape using mode switches and 10-turn potentiometer. Repeat for additional calibration points for NO_2 channel (i.e., 0.1, 0.2, 0.4, 0.5 ppm NO_2, etc.).
7. Return sample inlet line to sample manifold.

3.3 CALIBRATION PROCEDURE FOR BENDIX MODEL 8201 AMBIENT HYDROCARBON ANALYZER

ZERO

1. Place valves #1 and #2 to OFF position and meter/output switch to electrometer position.
2. Observe baseline while component gates are open (i.e., CH_4 light on and THC light on).
3. Adjust zero control for THC and CH_4 to zero by observing recorder output or meter while switched to appropriate output.
4. After one complete cycle adjust nonmethane zero control for zero indication on recorder or meter.
5. Return valves #1 and #2 to auto position.
6. Connect zero-air cylinder for dynamic zero utilizing calibrated capillary to appropriate flow rate of 200 cc/min. Switch operating mode switch to calibrate.
7. Compare readings with previous zero data and record. Any discrepancies indicate contaminated plumbing, regulator and/or cylinder of gas.

SPAN

1. Connect cylinder containing largest concentration to calibration inlet with correct flow rate of 200 cc/min.

   Caution: Avoid interchanging regulators and cylinders to prevent cross contamination.
2. After several cycles (at least two) set the span control for THC and CH_4 to the appropriate reading.
3. After completing span operation on THC and CH_4, switch output to electrometer position.

4. Observe strip chart for one cycle. Manually override valve #1 to the OFF position for the duration shown on the strip chart example. This will cause CH_4 output to be zero and cause the nonmethane output ($THC-CH_4$) to equal the THC output.
5. Adjust the nonmethane span control to the appropriate reading with the output switched to nonmethane.
6. Run additional calibration cylinders and record readings but do not adjust span controls.
7. Recheck nonmethane calibration as outlined above for each calibration level.

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4. Fontijn, A., A. J. Sabadell, and R. J. Ronco. Homogeneous Chemiluminescent Measurement of Nitric Oxide with Ozone. Anal Chem. 42: 575-579, May 1970.
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6. Federal Register. Ambient Air Quality Standards: Reference Method for Determination of Nitrogen Dioxide. Environmental Protection Agency. 38: 15174-15183, June 1973.
7. Ballard, L. F., J. B. Tommerdahl, C. E. Decker, T. M. Royal, and L. K. Matus. Field Evaluation of New Air Pollution Monitoring Systems: St. Louis Study, Phase I. Interim Report. Research Triangle Institute, Contract No. CPA 70-101, Environmental Protection Agency, 1971.
8. Decker, C. E., T. M. Royal, J. B. Tommerdahl, and L. K. Matus. Field Evaluation of New Air Pollution Monitoring Systems: St. Louis Study, Phase II. Interim Report. Research Triangle Institute, Contract CPA 70-101, Environmental Protection Agency, 1971.
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APPENDIX B

DATA TABULATION

Selected data collected at each site during the comparison period are summarized in tabular form in this section. These data generally correspond to the time frame when comparisons were made between the mobile and fixed site ozone analyzers at each of the four sites. Two data comparison periods are available from the Lewisburg and Garrett County sites and are included. Additional data are available from the mobile van at each site during the comparison period but were omitted when valid comparisons could not be made between ozone measurements from the fixed and mobile site analyzers. As previously stated, direct comparisons between nitrogen dioxide and hydrocarbon data from the fixed and mobile sites were not computed due to extremely low values obtained for nitrogen oxides at all sites and deficiency in the design of the Bendix 8201 hydrocarbon analyzer which invalidated all hydrocarbon measurements from the fixed stations.

The data in the following tables are hourly averages in $\mu g/m^3$. The instruments in the mobile unit and fixed sites are indicated by (M) and (F), respectively.

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R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
LEWISBURG, WEST VIRGINIA (AUGUST 29-31, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
August 29, 1973											
1	130	114	13	X	26	X	1,395	X	X	X	X
2	108	93	14	X	23	X	1,371	X	X	X	X
3	98	84	15	X	22	X	1,370	X	X	X	X
4	67	57	14	X	23	X	1,375	X	X	X	X
5	58	46	14	X	22	X	1,515	X	X	X	X
6	58	47	13	X	21	X	1,380	X	X	X	X
7	38	29	13	X	20	X	1,350	X	X	X	X
8	57	45	13	X	21	X	1,349	X	X	X	X
9	90	76	15	X	23	X	1,321	X	X	X	X
10	109	90	14	X	21	X	1,387	X	X	X	X
11	126	102	14	X	21	X	1,374	X	X	X	X
12	130	100	12	X	22	X	1,356	X	X	X	X
13	152	113	11	X	22	X	1,336	X	X	X	X
14	216	C	13	X	25	X	1,349	X	X	X	X
15	216	C	21	X	52	X	1,389	X	X	X	X
16	185	168	7	X	27	X	1,387	X	X	X	X
17	206	183	23	C	24	C	1,110	X	X	X	X
18	C	181	10	C	25	C	907	X	X	X	X
19	C	171	10	2	24	5	904	X	X	X	X
20	C	137	10	3	25	2	906	X	X	X	X
21	C	98	11	3	32	12	898	X	X	X	X
22	C	72	10	3	30	10	892	X	X	X	X
23	72	62	10	2	31	12	906	X	X	X	X
24	57	64	10	2	30	14	1,497	X	X	X	X

X	Analyzer in stabilization or not available
*	Data invalidated
C	Calibration
A	Data available only from stripcharts due to failure of computer
1	Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
LEWISBURG, WEST VIRGINIA (AUGUST 29-31, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
August 30, 1973											
1	45	53	9	2	28	4	1,440	X	X	X	X
2	33	40	11	2	27	4	1,446	X	X	X	X
3	31	39	10	2	27	2	1,420	X	X	X	X
4	31	40	9	2	26	1	1,391	X	X	X	X
5	22	31	11	2	18	1	1,408	X	X	X	X
6	25	34	11	2	17	1	1,386	X	X	X	X
7	30	38	11	2	16	1	1,347	X	X	X	X
8	25	33	11	2	16	1	1,338	X	X	X	X
9	32	39	10	2	18	2	1,331	X	X	X	X
10	47	C	11	3	17	1	1,280	X	X	X	X
11	47	50	30	7	20	5	1,236	X	X	X	X
12	80	78	34	14	31	22	C	X	X	X	X
13	158	168	16	2	20	15	C	X	X	X	C
14	184	198	13	2	20	4	C	X	X	X	C
15	189	204	12	2	18	5	C	X	X	X	C
16	173	194	14	2	18	10	C	X	X	X	0
17	185	186	C	15	C	4	1,390	X	X	X	0
18	150	162	C	1	C	27	1,346	X	X	X	0
19	145	157	C	3	C	2	1,331	X	X	X	0
20	160	177	14	3	18	2	1,316	X	X	X	0
21	184	211	6	4	18	3	1,304	X	X	X	0
22	183	204	5	3	21	13	1,285	X	X	X	0
23	108	118	5	4	22	7	1,268	X	X	X	0
24	73	84	6	3	19	2	1,241	X	X	X	0

X	Analyzer in stabilization or not available
*	Data invalidated
C	Calibration
A	Data available only from stripcharts due to failure of computer
1	Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
LEWISBURG, WEST VIRGINIA (AUGUST 29-31, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
August 31, 1973											
1	68	78	7	0	20	3	1,220	X	X	X	0
2	61	72	7	0	19	2	1,199	X	X	X	0
3	48	58	5	1	19	1	1,178	X	X	X	0
4	45	55	5	2	18	1	1,157	X	X	X	0
5	41	51	5	2	17	1	1,136	X	X	X	0
6	43	54	5	0	17	1	1,115	X	X	X	0
7	37	47	5	0	16	1	1,364	X	X	X	0
8	32	41	7	2	16	1	1,074	X	X	X	0
9	43	52	7	2	16	8	1,229	X	X	X	0

X Analyzer in stabilization or not available
* Data invalidated
C Calibration
A Data available only from stripcharts due to failure of computer
1 Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
KANE, PENNSYLVANIA (SEPTEMBER 6-8, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
HOUR	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
September 6, 1973											
1	142	155	5	X	13	X	A	A	A	X	X
2	138	154	6	X	11	X	A	A	A	X	X
3	137	154	5	X	10	X	A	A	A	X	X
4	125	138	5	X	13	X	A	A	A	X	X
5	121	133	5	X	13	X	A	A	A	X	X
6	114	127	4	X	14	X	A	A	A	X	X
7	107	116	4	X	19	X	A	A	A	X	X
8	103	110	5	X	19	X	A	A	A	X	X
9	102	109	4	X	16	X	A	A	A	X	X
10	98	105	4	C	13	X	A	A	A	X	X
11	90	95	5	C	12	C	A	A	A	X	X
12	101	111	5	C	13	C	A	A	A	X	X
13	117	133	3	C	17	C	A	A	A	X	X
14	133	152	4	2	10	12	A	A	A	X	X
15	142	165	4	2	10	12	A	A	A	X	X
16	147	173	3	2	11	13	A	A	A	X	X
17	C	169	3	1	10	12	A	A	A	X	X
18	C	165	C	3	C	13	A	A	A	X	X
19	C	186	3	2	13	15	A	A	A	X	X
20	C	196	2	1	19	23	A	A	A	X	X
21	C	171	1	1	24	29	A	A	A	X	X
22	C	C	1	1	19	22	A	A	A	X	X
23	C	C	1	1	14	17	A	A	A	X	X
24	161	C	C	C	C	C	A	A	A	X	X

X Analyzer in stabilization or not available
* Data invalidated
C Calibration
A Data available only from stripcharts due to failure of computer
1 Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
KANE, PENNSYLVANIA (SEPTEMBER 6-8, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
September 7, 1973											
1	145	171	C	C	C	C	A	A	A	X	X
2	139	165	2	3	5	10	A	A	A	X	X
3	133	160	2	2	3	6	A	A	A	X	X
4	120	144	1	2	3	5	A	A	A	X	X
5	116	138	2	2	3	7	A	A	A	X	X
6	93	109	1	2	9	19	A	A	A	X	X
7	78	92	1	2	9	19	A	A	A	X	X
8	37	43	7	7	24	49	A	A	A	X	X
9	45	53	9	7	17	33	A	A	A	X	X
10	69	85	3	2	4	7	A	A	A	X	X
11	84	103	3	2	1	4	A	A	A	X	X
12	88	106	4	4	3	10	A	A	A	X	X
13	96	117	14	8	6	1	A	A	A	X	X
14	99	120	4	2	2	9	A	A	A	X	X
15	104	125	3	2	1	4	A	A	A	X	X
16	121	147	3	1	1	4	A	A	A	X	X
17	131	158	3	2	2	7	A	A	A	X	X
18	127	153	4	2	4	10	A	A	A	X	X
19	121	144	3	1	2	7	A	A	A	X	X
20	118	140	2	1	5	12	A	A	A	X	X
21	102	120	2	1	7	17	A	A	A	X	X
22	104	121	2	1	5	11	A	A	A	X	X
23	124	147	2	1	5	10	A	A	A	X	X
24	133	154	1	1	4	8	A	A	A	X	X

X Analyzer in stabilization or not available
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C Calibration
A Data available only form stripcharts due to failure of computer
1 Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
KANE, PENNSYLVANIA (SEPTEMBER 6-8, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
September 8, 1973											
1	114	134	1	1	21	10	1,248	X	A	X	X
2	105	124	1	1	21	10	1,237	X	A	X	X
3	138	162	1	1	8	3	1,028	X	A	X	X
4	132	154	1	1	7	4	1,065	X	A	X	X
5	124	146	0	1	8	4	1,076	X	A	X	X
6	106	123	1	1	12	6	1,096	X	A	X	X
7	89	103	1	1	10	18	1,188	X	A	X	X
8	93	106	1	1	6	10	1,066	X	A	X	X
9	X	C	X	1	X	12	1,125	X	A	X	X
10	X	C	X	C	X	C	1,275	X	A	X	X
11	X	94	X	C	X	C	1,261	X	A	X	X
12	X	X	X	X	X	X	X	X	A	X	X

X	Analyzer in stabilization or not available
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C	Calibration
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1	Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
COSHOCTON, OHIO (SEPTEMBER 18-19, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
September 18, 1973											
1	X	131	A	A	14	1	1,054	X	X	X	0
2	X	74	A	A	16	0	1,058	X	X	156	0
3	X	58	A	A	16	0	1,057	X	X	90	0
4	X	54	A	A	19	0	X	X	X	90	0
5	X	51	A	A	20	1	1,064	X	X	175	2
6	X	37	A	A	21	1	1,068	X	X	193	2
7	X	41	A	A	15	0	1,052	X	X	98	4
8	X	51	A	A	14	1	1,025	X	X	126	2
9	X	50	A	A	14	0	1,011	X	X	81	0
10	C	50	A	A	14	0	1,026	X	X	106	0
11	C	46	A	A	14	0	1,024	X	X	51	0
12	C	46	A	A	16	0	1,031	X	X	100	0
13	C	*	A	A	16	*	*	X	X	*	*
14	63	78	A	A	16	10	1,016	X	X	95	0
15	76	88	A	A	15	9	1,000	X	X	100	0
16	66	X	A	A	15	X	X	X	X	X	X
17	83	X	A	A	17	X	X	X	X	X	X
18	100	106	A	A	19	5	1,000	X	X	50	5
19	103	119	A	A	18	0	1,008	987	21	80	5
20	96	111	A	A	17	0	1,007	968	39	173	4
21	94	112	A	A	16	0	1,001	990	11	102	17
22	91	108	A	A	14	0	990	981	9	66	15
23	85	102	A	A	14	0	1,016	975	41	90	13
24	98	110	A	A	14	0	1,021	950	71	90	12

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C Calibration
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1 Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
COSHOCTON, OHIO (SEPTEMBER 18-19, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
September 19, 1973											
1	89	102	A	A	14	0	1,025	987	38	61	13
2	79	88	A	A	16	0	1,065	997	68	74	13
3	73	79	A	A	16	0	1,031	994	37	136	14
4	72	79	A	A	19	0	1,040	998	42	78	47
5	65	70	A	A	20	0	1,040	1,017	23	36	27
6	68	74	A	A	21	0	1,031	1,019	12	121	33
7	51	51	A	A	15	0	1,059	1,016	43	106	14
8	24	21	A	A	14	0	1,144	1,056	88	152	11
9	20	17	A	A	14	0	1,209	1,114	95	129	5
10	20	16	A	A	14	C	C	C	X	C	C
11	28	22	A	A	14	C	C	C	X	C	C
12	73	C	A	A	16	C	C	C	X	C	C
13	91	97	A	A	16	C	C	C	X	C	C
14	X	X	A	A	X	X	X	X	X	X	X

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R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
GARRETT COUNTY, MARYLAND (SEPTEMBER 23-26 AND OCTOBER 2-3, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
September 23, 1973											
12	99	95	X	2	X	15	*	*	*	102	33
13	111	106	X	2	X	10	*	*	*	121	17
14	118	110	X	2	X	7	*	*	*	144	9
15	149	137	X	1	X	5	*	*	*	60	5
16	156	141	X	2	X	4	*	*	*	62	1
17	166	148	X	1	X	4	1064	1055	9	96	0
18	171	150	X	1	X	5	1098	1042	56	136	11
19	162	146	X	1	X	6	1091	1031	60	126	27
20	156	143	X	1	X	6	*	*	*	76	23
21	156	145	X	1	X	5	*	*	*	35	18
22	150	141	X	1	X	7	1078	1031	47	117	50
23	142	134	X	1	X	9	1060	1027	23	92	61
24	112	107	X	1	X	28	*	*	*	50	132
September 24, 1973											
1	138	133	X	1	X	9	1053	1024	29	106	49
2	155	149	X	1	X	4	*	*	*	78	16
3	158	154	X	1	X	3	1038	1021	17	93	6
4	155	150	X	1	X	2	*	*	*	112	0
5	144	140	X	1	X	4	1038	999	39	118	1
6	138	132	X	2	X	6	*	*	*	108	10
7	160	153	X	1	X	3	1026	981	45	110	34
8	159	154	X	1	X	2	*	*	*	66	12
9	153	145	X	1	X	2	*	*	*	140	5
10	143	132	X	2	X	3	1046	967	79	115	2
11	150	137	X	2	X	6	X	X	X	X	19

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R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
GARRETT COUNTY, MARYLAND (SEPTEMBER 23-26 AND OCTOBER 2-3, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
September 24, 1973											
12	103	93	X	10	X	60					
13	150	133	X	4	X	23	X	X	X	X	286
14	159	139	X	2	X	4	C	C	C	C	97
15	161	141	X	2	X	2	1218	1033		106	11
16	C	150	X	2	X	3	*	*	*	88	0
17	C	146	X	0	X	3	*	*	*	68	0
18	C	144	X	1	X	4	*	*	*	47	0
19	161	141	X	2	X	3	*	*	*	113	0
20	169	157	X	2	X	17	*	*	*	88	0
21	162	153	X	2	X	14	1030	995	35	177	64
22	160	151	X	2	X	9	*	*	*	112	38
23	143	136	X	2	X	6	*	*	*	62	14
24	144	138	X	2	X	8	*	*	*	103	1
							*	*	*	122	
September 25, 1973											
1	135	128	X	2	X	8					
2	132	127	X	2	X	8	*	*	*	117	41
3	129	124	X	2	X	5	*	*	*	122	30
4	115	112	X	1	X	6	*	*	*	98	0
5	114	111	X	1	X	5	*	*	*	138	0
6	110	107	X	1	X	6	*	*	*	109	0
7	104	101	X	0	X	7	*	*	*	116	0
8	91	90	X	0	X	8	*	*	*	147	0
9	96	T	X	1	X	11	1063	1049	14	176	1
10	96	T	X	2	X	15	X	X	X	242	5
11	108	111	X	2	X	14	1102	1075	127	216	34
							C	C	C	C	34

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R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
GARRETT COUNTY, MARYLAND (SEPTEMBER 23-26 AND OCTOBER 2-3, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
September 25, 1973											
12	114	117	X	2	X	16	1075	1011	64	205	30
13	129	132	X	2	X	12	1064	998	66	192	11
14	137	140	X	2	X	10	1057	1005	52	172	C
15	153	C	X	1	X	7	1043	994	49	151	1
16	152	C	X	2	X	10	C	C	C	C	1
17	154	149	X	C	X	C	C	C	C	C	6
18	154	149	X	2	X	13	*	*	*	175	6
19	145	141	X	3	X	17	1044	1042	2	288	9
20	132	132	X	2	X	20	*	*	*	184	26
21	132	132	X	2	X	19	*	*	*	267	22
22	140	140	X	2	X	13	*	*	*	218	1
23	132	134	X	2	X	14	*	*	*	191	9
24	133	135	X	2	X	12	*	*	*	205	4
September 26, 1973											
1	137	142	X	2	X	9	*	*	*	126	2
2	142	146	X	2	X	8	*	*	*	158	1
3	141	146	X	3	X	5	*	*	*	170	1
4	137	143	X	2	X	6	*	*	*	135	1
5	129	135	X	2	X	6	*	*	*	161	1
6	121	127	X	2	X	6	*	*	*	106	1

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R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
GARRETT COUNTY, MARYLAND (SEPTEMBER 23-26 AND OCTOBER 2-3, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
October 2, 1973											
12	C	61	X	C	X	C	988	992	6	124	X
13	C	67	X	C	X	C	1018	990	28	77	X
14	76	74	X	2	X	5	987	987	0	124	X
15											
16	80	79	X	2	X	4	*	*	*	55	X
17	75	70	X	2	X	6	*	*	*	92	X
18	69	63	X	2	X	7	*	*	*	38	X
19	62	56	X	2	X	7	*	*	*	81	X
20	48	43	X	1	X	17	*	*	*	59	X
21	50	51	X	1	X	9	*	*	*	61	X
22	55	59	X	1	X	6	*	*	*	69	X
23	62	65	X	1	X	3	*	*	*	83	X
24	72	77	X	1	X	2	*	*	*	85	X
October 3, 1973											
1	77	82	X	1	X	3	1017	1017	0	38	X
2	77	83	X	1	X	3	1033	1026	7	83	X
3	71	76	X	1	X	3	1048	1034	14	62	X
4	74	80	X	1	X	4	1039	1020	19	77	X
5	90	89	X	1	X	4	*	*	*	90	X
6	94	92	X	1	X	3	1017	1017	0	57	X
7	85	83	X	1	X	6	1022	1021	1	91	X
8	79	77	X	2	X	7	1030	1030	0	91	X
9	71	70	X	1	X	5	1050	1032	18	94	X
10	87	87	X	2	X	6	1359	1035	324	120	X
11	106	100	X	2	X	4	1035	1035	0	99	X
12	123	116	X	C	X	C	C	C	C	C	X
13	133	124	X	C	X	C	1070	1044	26	76	X
14	137	127	X	1	X	14	1065	1054	11	92	X

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1 Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
LEWISBURG, WEST VIRGINIA (OCTOBER 5-8, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
October 5, 1973											
13	X	C	X	X	X	X	1,087	1,005	82	101	
14	X	C	X	X	X	X	1,117	1,008	109	120	
15	X	C	X	C	X	C	1,113	1,001	112	87	
16	X	C	X	X	X	X	C	C	C	C	
17	122	117	*	C	*	C	1,069	995	74	72	
18	111	118	5	1	12	4	1,117	992	125	138	
19	106	112	9	1	7	7	1,073	1,007	66	94	
20	106	113	7	1	5	7	1,106	1,005	101	116	
21	91	*	9	*	4	*	*	*	*	120	
22	65	66	12	1	4	13	1,176	1,090	86	80	
23	77	82	7	1	4	6	1,155	1,047	108	109	
24	57	59	8	1	3	10	1,150	1,066	84	76	
October 6, 1973											
1	55	57	6	0	1	6	1,146	1,080	66	103	
2	47	49	5	1	3	3	1,152	1,078	74	72	
3	41	41	4	0	1	4	1,157	1,093	64	74	
4	41	43	3	0	2	1	1,153	1,068	85	88	
5	29	29	4	0	0	3	1,189	1,119	70	85	
6	29	30	4	1	0	3	1,180	1,104	76	94	
7	30	31	4	1	0	4	1,168	1,091	77	83	
8	24	24	4	1	1	3	1,160	1,093	67	64	
9	27	27	3	1	3	4	1,171	1,073	98	87	
10	40	41	3	1	7	5	1,110	1,057	53	90	
11	65	70	5	1	6	3	1,102	1,033	69	67	
12	84	90	9	2	6	14	1,094	1,011	83	82	

X Analyzer in stabilzation
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R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
LEWISBURG, WEST VIRGINIA (OCTOBER 5-8, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
October 6, 1973 continued											
13	100	107	5	1	5	7	1,083	1,010	73	98	
14	105	113	8	2	8	13	1,088	1,002	86	168	
15	115	124	9	1	9	12	1,068	1,001	67	112	
16		135	4	0	8	7	1,058	997	61	76	
17	130	140	4	0	5	4	1,069	997	72	77	
18	130	140	6	0	2	8	1,061	998	63	154	
19	130	142	8	0	0	9	1,078	1,010	68	79	
20	117	127	7	0	2	7	1,067	1,008	59	89	
21	98	104	9	0	2	12	1,109	1,033	76	87	
22	76	79	13	0	0	20	1,153	1,072	81	106	
23	66	68	8	0	0	14	1,148	1,080	68	89	
24	62	65	7	0	2	11	1,175	1,072	103	88	

X	Analyzer in stabilization
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1	Mobile site

R.T.I. EASTERN REGIONAL OZONE STUDY
QUALITY ASSURANCE PROGRAM
LEWISBURG, WEST VIRGINIA (OCTOBER 5-8, 1973)
Hourly Average Data Summary
(concentration in micrograms per cubic meter)

HOUR	OZONE		NITRIC OXIDE		NITROGEN DIOXIDE		HYDROCARBONS[1] (BECKMAN ANALYZER)			CARBON MONOXIDE[1] (BECKMAN ANALYZER)	TOTAL SULFUR[1]
	FIXED	MOBILE	FIXED	MOBILE	FIXED	MOBILE	TOTAL	METHANE	NONMETHANE		
October 7, 1973											
1	59	62	5	0	1	6	1,137	1,070	67	67	X
2	52	54	3	0	0	5	1,134	1,075	59	70	X
3	47	48	4	0	1	3	1,139	1,067	72	153	X
4	44	46	2	0	1	2	1,133	1,076	57	69	X
5	44	45	2	1	1	2	1,126	1,063	63	68	X
6	44	44	3	0	1	2	1,106	1,049	57	80	X
7	40	40	1	0	1	1	1,132	1,052	80	75	X
8	45	46	2	0	1	2	1,096	1,036	60	78	X
9	46	47	3	0	2	1	1,079	1,031	148	63	X
10	58	62	0	0	6	3	1,084	1,009	75	101	X
11	59	60	3	0	4	2	X	X	X	C	X
12	76	71	2	1	7	2	X	X	X	C	X
13	99	105	2	1	8	6	C	C	C	C	X
14	103	109	3	1	6	8	C	C	C	C	X
15	117	124	2	0	7	9	C	C	C	C	X
16	135	142	2	1	12	4	1,030	1,028	2	80	X
17	128	138	3	1	12	6	*	*	*	79	X
18	134	142	3	1	11	6	*	*	*	81	X
19	127	136	6	1	10	11	*	*	*	97	X
20	99	106	12	2	8	22	*	*	*	147	X
21	92	98	9	1	10	13	1,127	1,084	44	138	X
22	70	76	14	1	9	25	1,176	1,152	24	234	X
23	71	74	8	1	9	13	1,165	1,128	37	142	X
24	58	59	8	1	9	13	*	*	*	122	X

X Analyzer in stabilization
* Data invalidated
C Calibration
A Data available only from stripcharts due to failure of computer
1 Mobile site

INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN EASTERN UNITED STATES

Part 3. Airborne Ozone Monitoring Program

by

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Quality Assurance and Environmental Monitoring Laboratory
National Environmental Research Center

Prepared for

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Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, N. C. 27711

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1.0 INTRODUCTION

During the period of July through October, 1973, the Research Triangle Institute conducted an investigation of ozone (O_3) and O_3 precursor concentrations at nonurban locations in the eastern United States under EPA Contract 68-02-1077, RTI Project 41U-848. This field program was designed to evaluate the occurrence and significance of high O_3 concentrations at nonurban locations. The program consisted of the measurement of O_3, nitrogen dioxide and nonmethane hydrocarbons at three of the four sampling sites; ozone only was measured at the fourth site.

The purpose of the airborne O_3 monitoring program was to collect supplementary air quality data; i.e., measurements of concentrations of ozone above the ground within the geographic region of the fixed monitoring stations established under Contract 68-02-1077.

A solid phase O_3 analyzer with support equipment was installed in a C-45 aircraft supplied by the National Environmental Research Center - Las Vegas. Data validation consisted basically of ground calibrations performed with the equipment installed in the aircraft, and confirmed by making low altitude passes at each of the monitoring sites when weather conditions permitted. Data from airborne instruments were compared with fixed station values for the respective times. Data were collected over a flight path which covered the route from Raleigh, N.C., to Lewisburg, W.Va., to Garrett County, Md., to Kane, Pa., to Coshocton, Ohio, and return to Raleigh, N.C. Vertical descents in 2000 ft (610 m) increments were made over each of the ground stations as weather conditions permitted.

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2.0 MEASUREMENT SYSTEM

2.1 Aircraft System

The measurement system consisted of a solid phase chemiluminescent O_3 monitor installed in a C-45 aircraft. The aircraft and pilot were furnished by the NERC-LV. The aircraft is shown in Figure 1.

The C-45 (Beechcraft) has a cruising speed of 150 knots, a minimum speed of 95 knots, climb rate of 500 ft/min, turning radius of 1-1/4 mile, useful load above pilot and fuel of 1600 lbs and a range of 5-1/2 hrs or 880 miles (1416 km) at cruise speed. Navigation equipment included 2 VOR units with DME, ADF, and Flux-gate Compass.

The air intake probe visible in Figure 1 was approximately 12 ft (3.6 m) in length and coupled into an expansion cone inside the cabin, which effectively slowed the air velocity by a factor of 10/1. The intake air was vented directly into the cabin. The analyzer sample inlet line was located near the center of the expansion cone at the outlet end.

The O_3 meter was mounted on shockmounts and bolted to a shelf just aft of the pilot's compartment on the port side of the aircraft. The instrument is shown installed in Figure 2. Other equipment in view in Figure 2 includes a strip chart recorder for data collection, mass flow meter and digital voltmeter for precise output voltage measurements.

Power for the instrumentation was supplied by an inverter (28 Vdc to 115 V 60 Hz) which was connected to the aircraft's primary power bus. Two inverters were available, one as a standby in case of failure of the other unit. These units were supplied with the aircraft. A block diagram showing the configuration at the instrumentation is given in Figure 3.

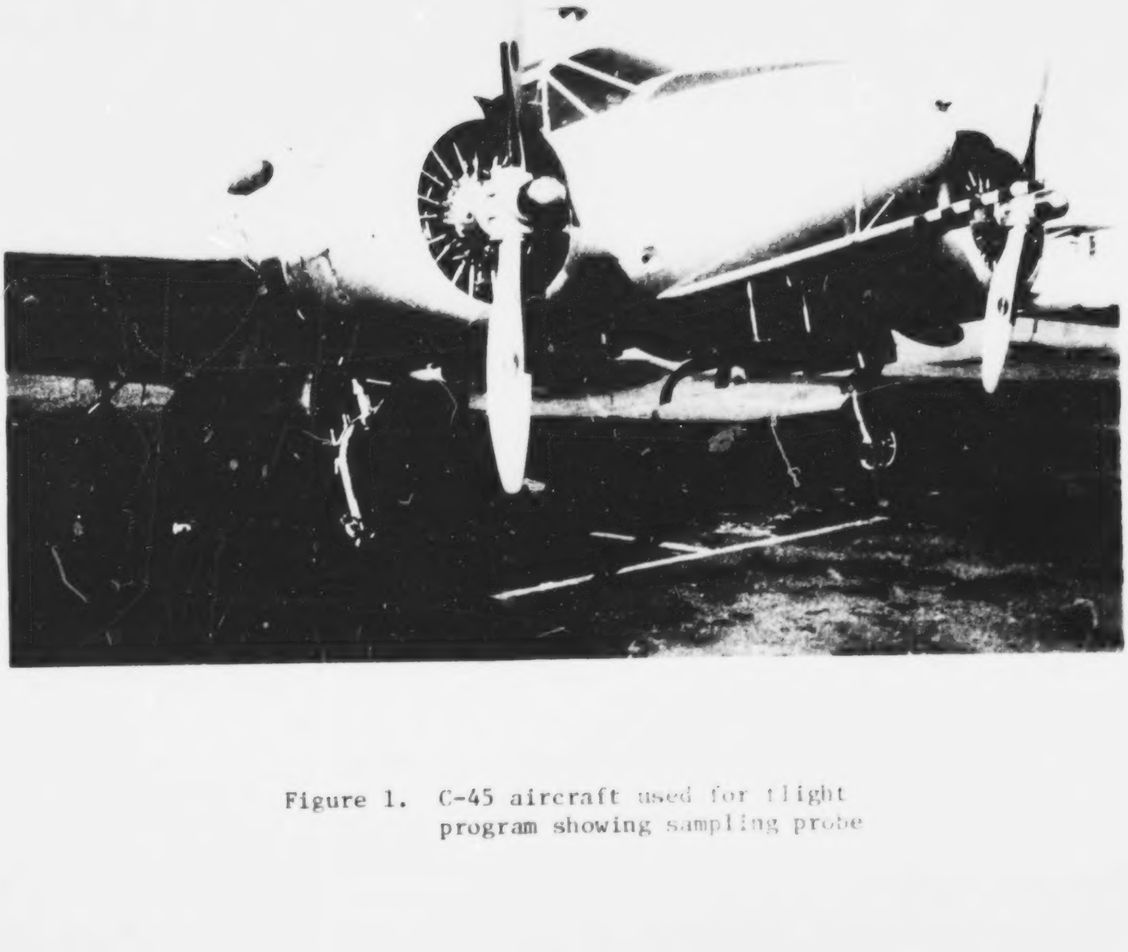


Figure 1. C-45 aircraft used for flight
program showing sampling probe

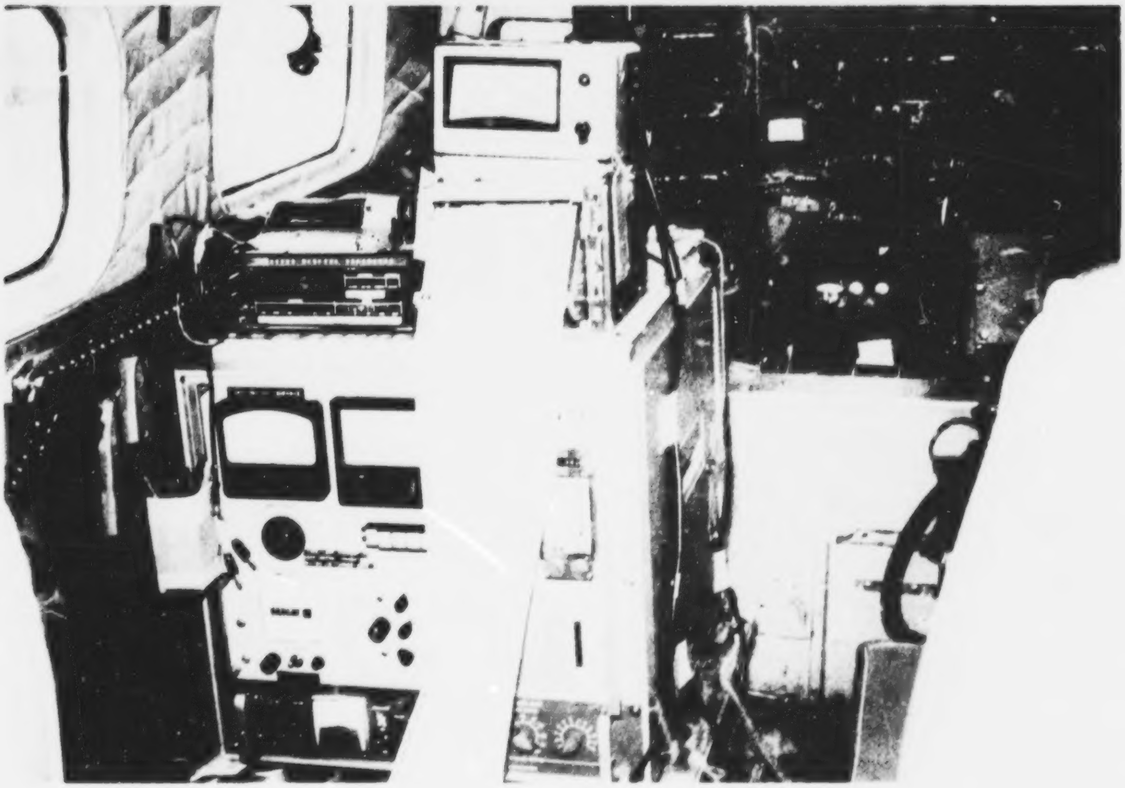


Figure 2. Instrumentation for airborne ozone measurement program

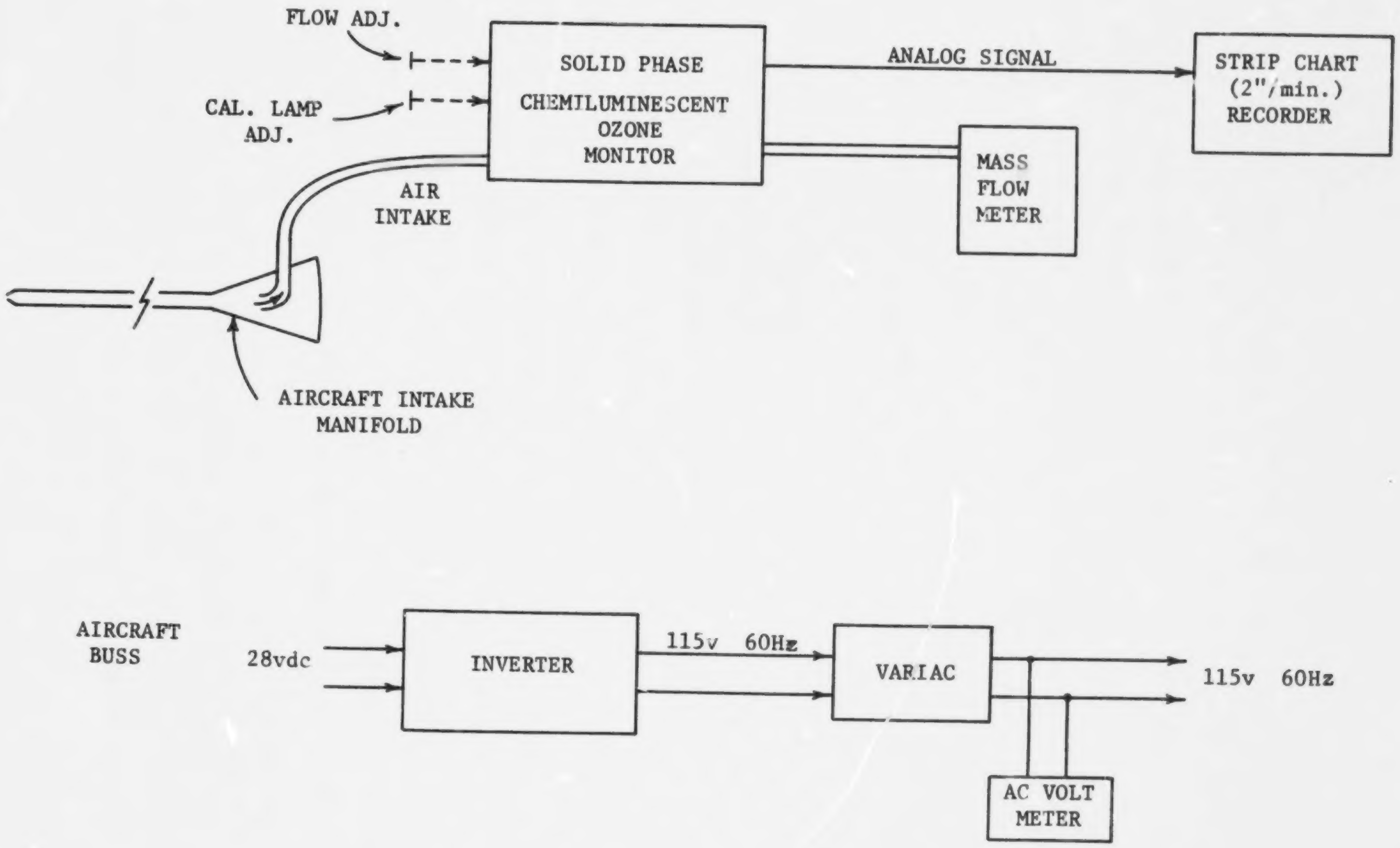

FLOW ADJ.
CAL. LAMP ADJ.
SOLID PHASE CHEMILUMINESCENT OZONE MONITOR
ANALOG SIGNAL
STRIP CHART (2"/min.) RECORDER
AIR INTAKE
MASS FLOW METER
AIRCRAFT INTAKE MANIFOLD
AIRCRAFT BUSS
28vdc
INVERTER
115v 60Hz
VARIAC
115v 60Hz
AC VOLT METER

Figure 3. Block diagram of instrumentation system

2.2 Ozone Analyzer

The O_3 analyzer utilizes the rhodamine B chemiluminescent disc as the basic sensor and a photomultiplier tube for collecting and amplifying the emitted light. As air containing O_3 is passed over the disc, a reaction between the O_3 and the organic compound or dye imbedded on the disc takes place and light is emitted. The amount of light emitted is directly proportioned to the concentration of O_3. The design and operational characterization are described in Reference 1.

A functional diagram of the O_3 meter is shown in Figure 4. The system has three modes of operation: measure, purge and calibrate. In the measure mode, the inlet air is passed directly to the detection chamber and the O_3 detected; in the purge mode, the inlet air is first passed through a clean up filter which removes water vapor and other contaminants and destroys any O_3 present before it passes through the detection chamber; in the calibrate mode, the unit operates in the purge configuration but a controlled amount of O_3 is generated in the "clean air" as it passes through the calibration unit by exposing the air stream to a UV light source. A calibrated aperture control facilitates varying the O_3 concentration and a front panel control and meter provides for lamp current control and monitoring, respectively. The light emitted from the disc is detected by a photo-multiplier tube, amplified and displayed on a strip chart recorder.

A typical output signal is illustrated in Figure 5, as measured during one of the flights. A calibration signal appears once per cycle and is used as follows in determining the value of the measure signal:

$$O_3 \text{ concentration in ppm} = ck \, \frac{\text{measure value in mV}}{\text{calibrate value in mV}}$$

where k is a correction factor which is a function of the ambient pres-

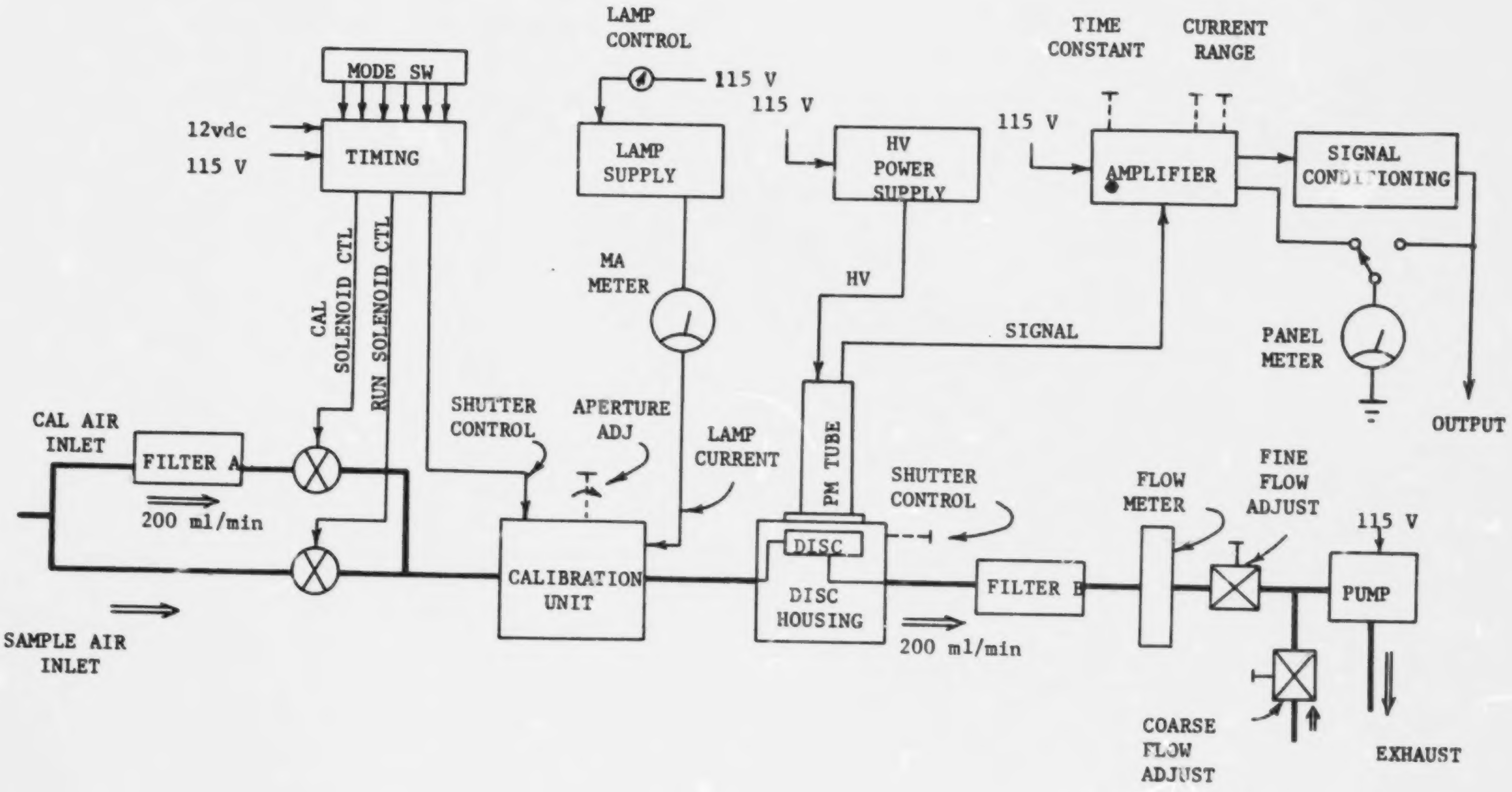

LAMP CONTROL
115 V
115 V
TIME CONSTANT
CURRENT RANGE
115 V
MODE SW
12vdc
115 V
TIMING
LAMP SUPPLY
HV POWER SUPPLY
AMPLIFIER
SIGNAL CONDITIONING
CAL SOLENOID CTL
RUN SOLENOID CTL
MA METER
HV
SIGNAL
PANEL METER
OUTPUT
CAL AIR INLET
FILTER A
200 ml/min
SHUTTER CONTROL
APERTURE ADJ
LAMP CURRENT
PM TUBE
SHUTTER CONTROL
FLOW METER
FINE FLOW ADJUST
115 V
DISC
CALIBRATION UNIT
DISC HOUSING
FILTER B
PUMP
SAMPLE AIR INLET
200 ml/min
COARSE FLOW ADJUST
EXHAUST

Figure 4. Ozone meter functional diagram

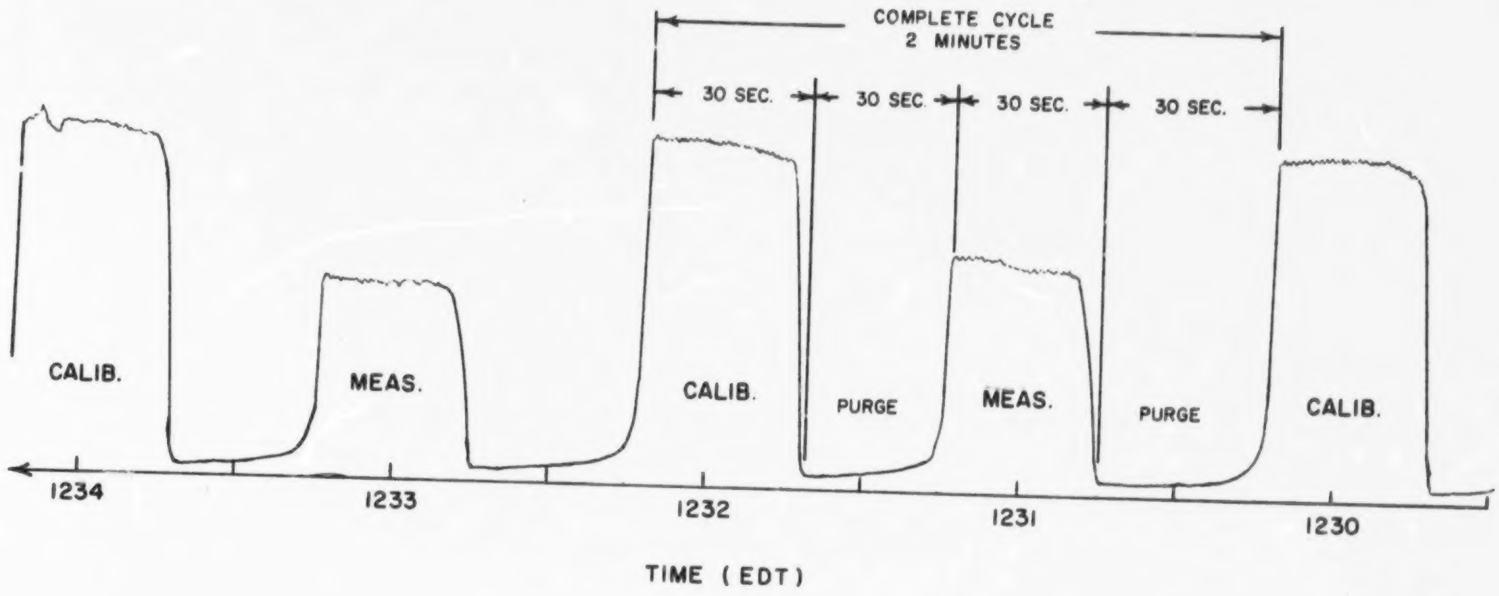


Figure 5. Typical signal outputs for solid phase ozone meter

sure or altitude and c is the calibrate value in ppm determined by standard calibration procedure.

As may be noted from Figure 5, the instrument is in the measure mode 25% of the time. The value of each calibrate and measure signal is obtained by using the amplitude of the signal minus the preceding purge value; thus, the drift of the instrument is accounted for each cycle. The response time of the instrument was essentially limited by the response time of the strip chart recorder, which has a response of 1/2 sec full scale, when the analyzer amplifier time constant control is operated in its "normal" setting.

Comparisons and evaluations have been made previously between the gas-phase chemiluminescent and the solid-phase chemiluminescent O_3 analyzer under field conditions, see References 2, 3.

2.3 Calibration

The analyzer was calibrated in the laboratory before installation and again after it was removed from the aircraft. In addition, in-situ calibrations were performed on the ground just prior to data flights with the analyzer installed and operating off of a ground based power supply. The calibration unit used was a portable O_3 source which utilized a UV lamp for generation of known concentrations of O_3, referenced to the neutral-buffered KI procedure (as published in Federal Register, April 30, 1971, Edition). O_3 output at the source manifold was controlled by maintaining a constant mass flow of air through the quartz tube and a constant UV lamp current. A flow rate greater than the sampling requirements of the analyzer was maintained.

The O_3 analyzer incorporated an internal calibration unit which uses the radiation flux from a UV lamp for generation of O_3. It has been determined that if the UV radiation flux is held constant (i.e., maintaining constant lamp current) the ratio of O_3 to O_2 is constant for a given volumetric flow rate. Therefore, by maintaining a given volumetric flow rate or knowing the flow rate, the O_3 concentration in ppm may be determined for any altitude or pressure.

Because of various factors, it was not feasible to maintain constant volumetric flow at all altitudes, but constant mass flow was obtained by using a mass flow meter in the gas line of the instrument and adjusting for a pre-selected mass flow rate at each altitude. Tests were conducted in flight to determine the volumetric flow rate at the various altitudes with a fixed mass flow rate of 200 cc/min. These were checked several times with a bubble flow meter to test the repeatability of the method. It was not feasible to use a bubble flow meter on descents over a station during a data collection flight because the time period at each altitude was too short. A couple of test flights were flown to check out the operation at the lower altitudes in areas suitable to this type of flight.

Tests were performed in the laboratory on the analyzer which had been flown to determine the ozone concentration generated by the internal calibrate unit for volumetric flow rates over the range of interest. This was done by varying the flow rate in the O_3 analyzer and measuring the O_3 concentrations in the calibrate mode against a known concentration established in an external manifold. This, then, yielded a value for the internal calibration unit corresponding to each altitude or volumetric flow rate of interest.

3.0 DATA COLLECTION PROCEDURE

The normal flight procedure was to warm-up the equipment, run the calibration checks and be ready for take-off from the Raleigh-Durham airport around 0900. The equipment was turned off during take-off due to power requirements of the aircraft and turned on immediately after clearing the field. The equipment was allowed to stabilize for approximately 30 minutes after take-off.

The flight path was, in general, as shown in Figure 6. A constant altitude was maintained between sampling sites, and cruising speed was 150 knots. Standard airway routes were flown with some deviation under VFR conditions. The use of the VOR radials and the DME allowed for fairly precise position location in addition to visual checks over identifiable points.

Upon reaching a sampling station, descent in 2000 feet (610 m) increments were made; at each altitude, the aircraft was leveled off and a circular or race-track pattern was flown for approximately 5 minutes or until at least two data points were obtained. A 50 ft (15.2 m) pass over the runway was made at the Greenbrier Valley Airport and the Garrett County Airport to obtain a data point as near as practical to the sampling station. The descent pattern was flown (approximately 8 km) to the NW of the Greenbrier Valley Airport and around the Garrett County Airport. At the Kane, Pa. sampling site, the lowest altitude was approximately 600 ft (183 m) above the terrain and the flight pattern was around the perimeter of the town. The circular flight patterns were such that a full 360° was usually completed in approximately 5 minutes.

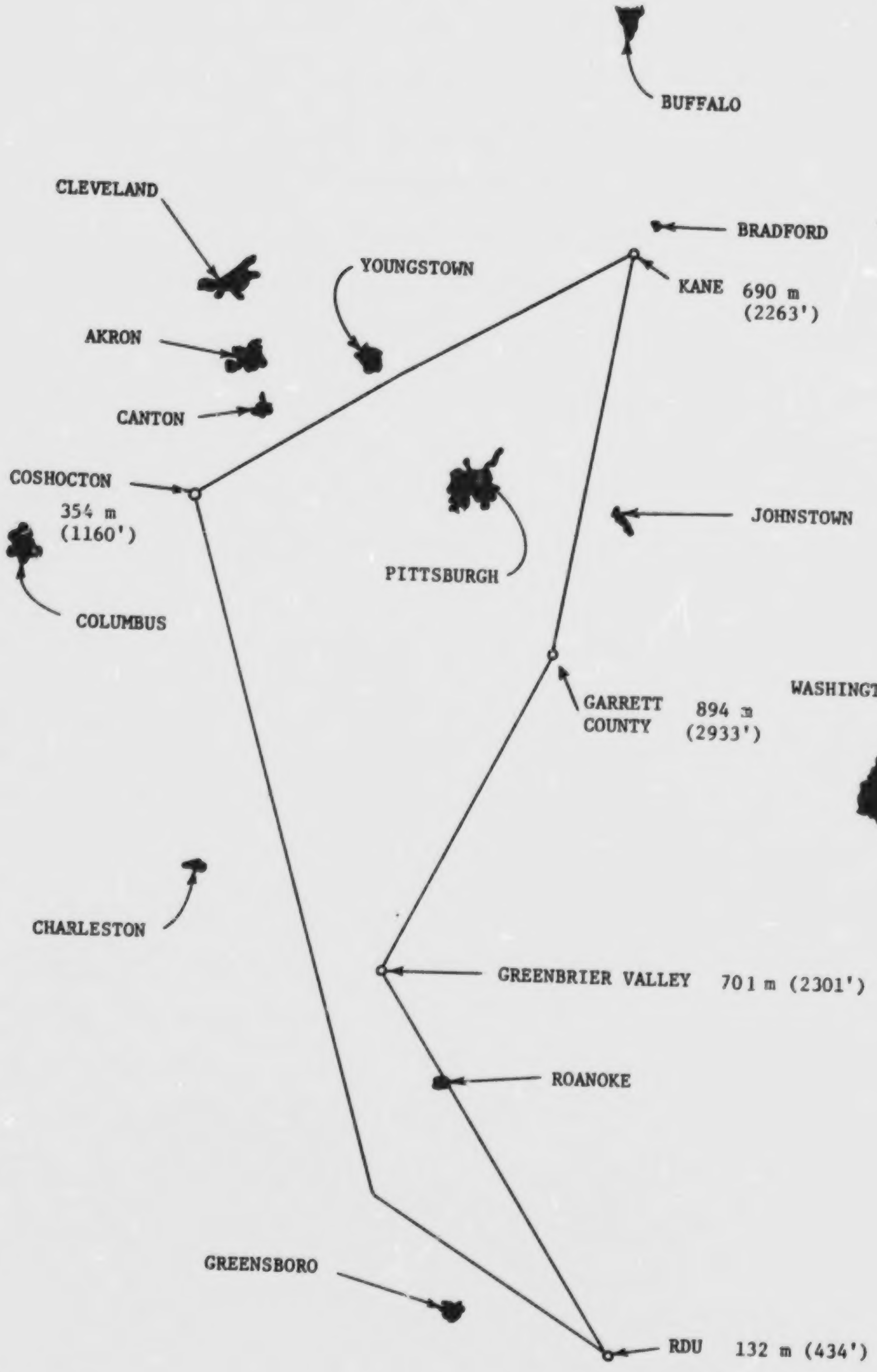

BUFFALO
CLEVELAND
BRADFORD
YOUNGSTOWN
KANE 690 m (2263')
AKRON
CANTON
COSHOCTON
354 m (1160')
JOHNSTOWN
PITTSBURGH
COLUMBUS
GARRETT COUNTY 894 m (2933')
WASHINGTON
CHARLESTON
GREENBRIER VALLEY 701 m (2301')
ROANOKE
GREENSBORO
RDU 132 m (434')

Figure 6. General flight path showing elevation above MSL of the fixed sampling stations

The flight pattern over the Coshocton, Ohio site consisted of flying a VOR vector so that a straight ground track was flown for this site Straight and level flight at each altitude was approximately 5 minutes with the sampling station near the center of the ground track. Descent over the station was limited to approximately 600 ft above the terrain under VFR (visual flight rules) conditions.

Refueling stops were made at Bradford, Pennsylvania just after the descent over the Kane, Pennsylvania sampling site. The total flying time required for one full circuit was approximately 7-1/4 hours. The program flying time required a total of 26 hours which included test flights for equipment procedure check-out and the data acquisition flights.

4.0 DATA

Data are presented in the following formats as available for the data acquisition flights of August 8 and September 11-12, 1973.

a) Ground track plot - showing relative locations of cities and sampling stations. Ozone concentrations and time are superimposed on the ground track for the flight. Altitude for each leg of the flight is also shown.

b) Elevation plot - showing relative elevation of the ground track above MSL in the lower plot and ozone concentration with respect to time and location in the upper plot.

c) Vertical sounding - showing the ozone concentration versus altitude over the sampling sites. Ground elevation and data points for the three 15 min averages which bracket the time when the closest approach data point were obtained.

d) Sampling site data - for period of 0700 to 1800 for the flight day, showing the time that the aircraft was over the station.

e) Strip chart data - examples of rapidly varying ozone concentrations.

The flight altitudes and ground elevation above mean sea level (MSL) are presented in feet and meters since the aircraft altimeter, the assigned flight altitudes and navigation chart data are given in feet. The altitudes given are nominal values since there is some error in the altimeter and some variations in flight altitude over short periods of time. All of the ozone contration data are given in $\mu g/m^3$ at standard conditions. The altitudes at which the measurements were made may be obtained from the respective figures.

4.1 Data Acquisition Flight for August 8, 1973

The flight log was as follows:

a) Flight was started under VFR conditions, increasing cloud cover required subsequent increases in altitude; unable to descend over Greenbrier Valley Airport because of low visibility; climbed to 11,900 ft to get into clear and file IFR flight plan, unable to maintain flow rate at this altitude, therefore, no valid data; rest of flight was made under IFR conditions.

b) Flew over Kane, Pa. sampling site, approximately 2000 ft above terrain, data checked quite closely with data observed by calibration crew at the sampling station.

c) Flight to Coshocton, Ohio was aborted near Youngstown, Ohio due to engine failure; emergency landing was made at Akron-Canton Regional Airport.

Data for the flight are presented in Figures 7, 8, and 9. Ozone concentration for the fixed sites for the same date are given in Figure 10. Two illustrations of changing ozone concentrations are given in the strip chart tracings in Figures 11 and 12.

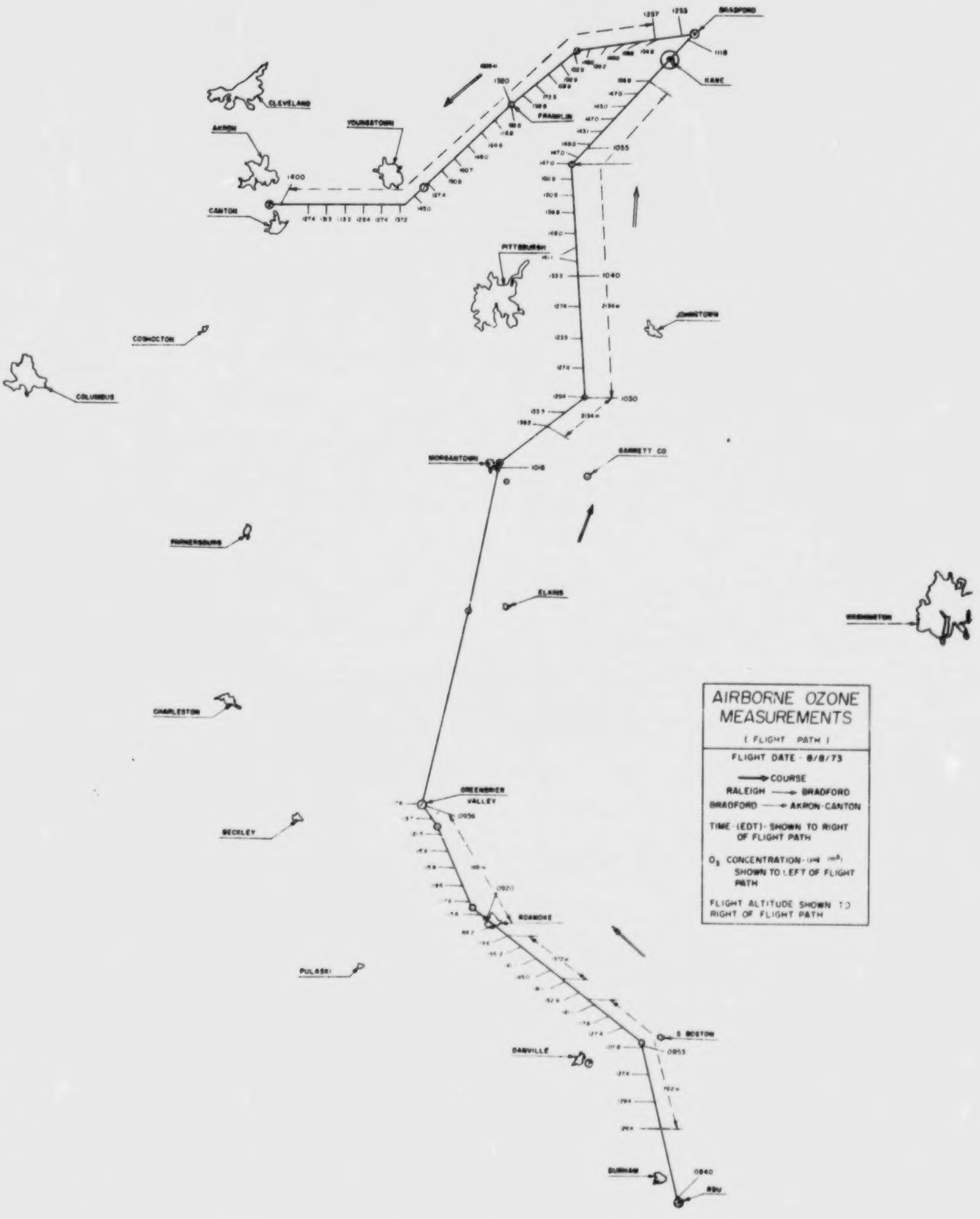

AIRBORNE OZONE MEASUREMENTS
(FLIGHT PATH)
FLIGHT DATE - 9/8/73
COURSE
RALEIGH → BRADFORD
BRADFORD → AKRON-CANTON
TIME (EDT) SHOWN TO RIGHT OF FLIGHT PATH
O3 CONCENTRATION (μg/m³) SHOWN TO LEFT OF FLIGHT PATH
FLIGHT ALTITUDE SHOWN TO RIGHT OF FLIGHT PATH
BRADFORD
KANE
FRANKLIN
CLEVELAND
AKRON
YOUNGSTOWN
CANTON
PITTSBURGH
JOHNSTOWN
COSHOCTON
COLUMBUS
MORGANTOWN
GARRETT CO
PARKERSBURG
ELKINS
WASHINGTON
CHARLESTON
GREENBRIER VALLEY
BECKLEY
ROANOKE
PULASKI
S BOSTON
DANVILLE
DURHAM
RDU
1400
1320
1257
1255
1118
1055
1040
1030
1016
0936
0920
0853
0840
2134 m

Figure 7. September 8, 1973 data acquisition flight.

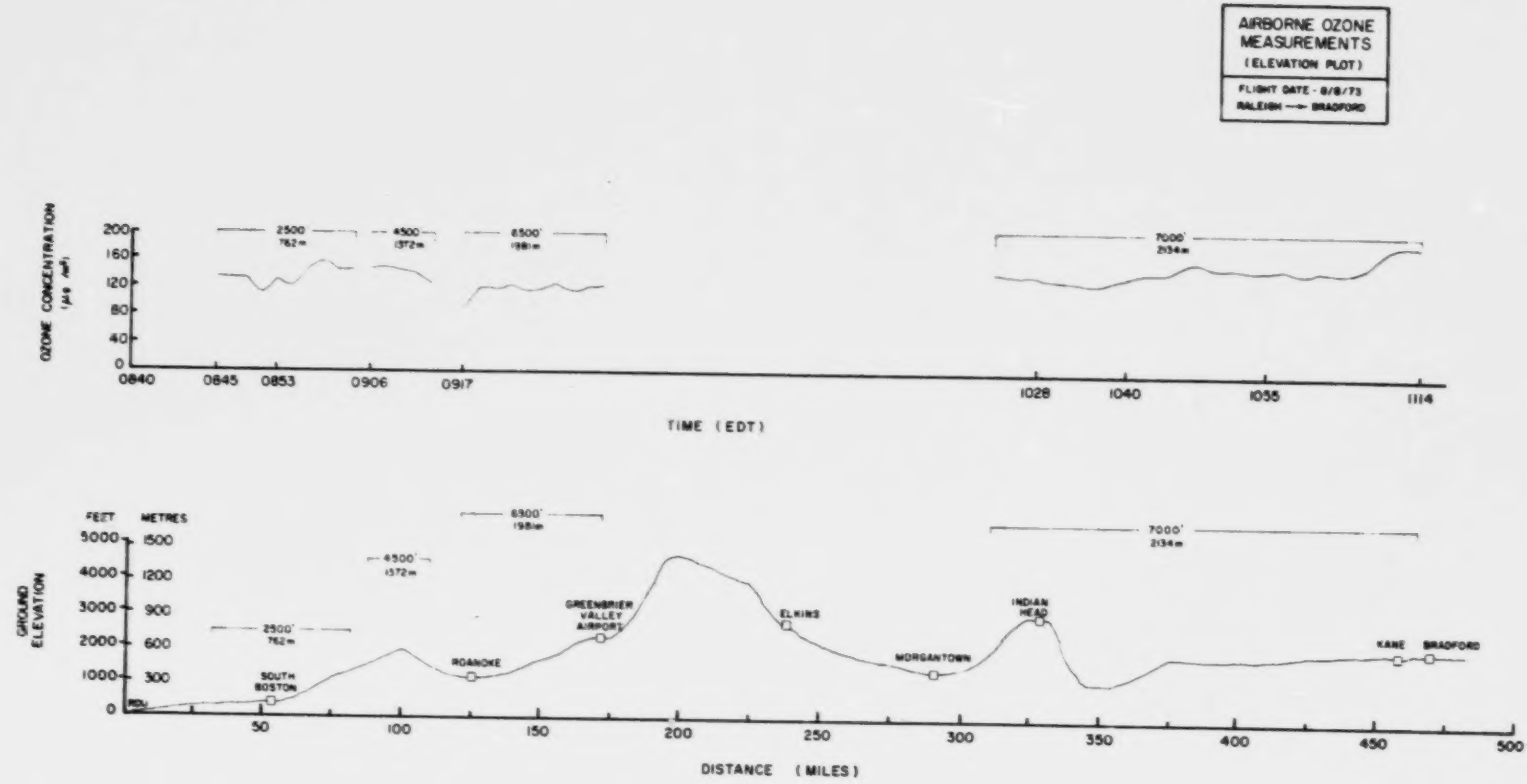


Figure 8. September 8, 1973, data acquisition flight.

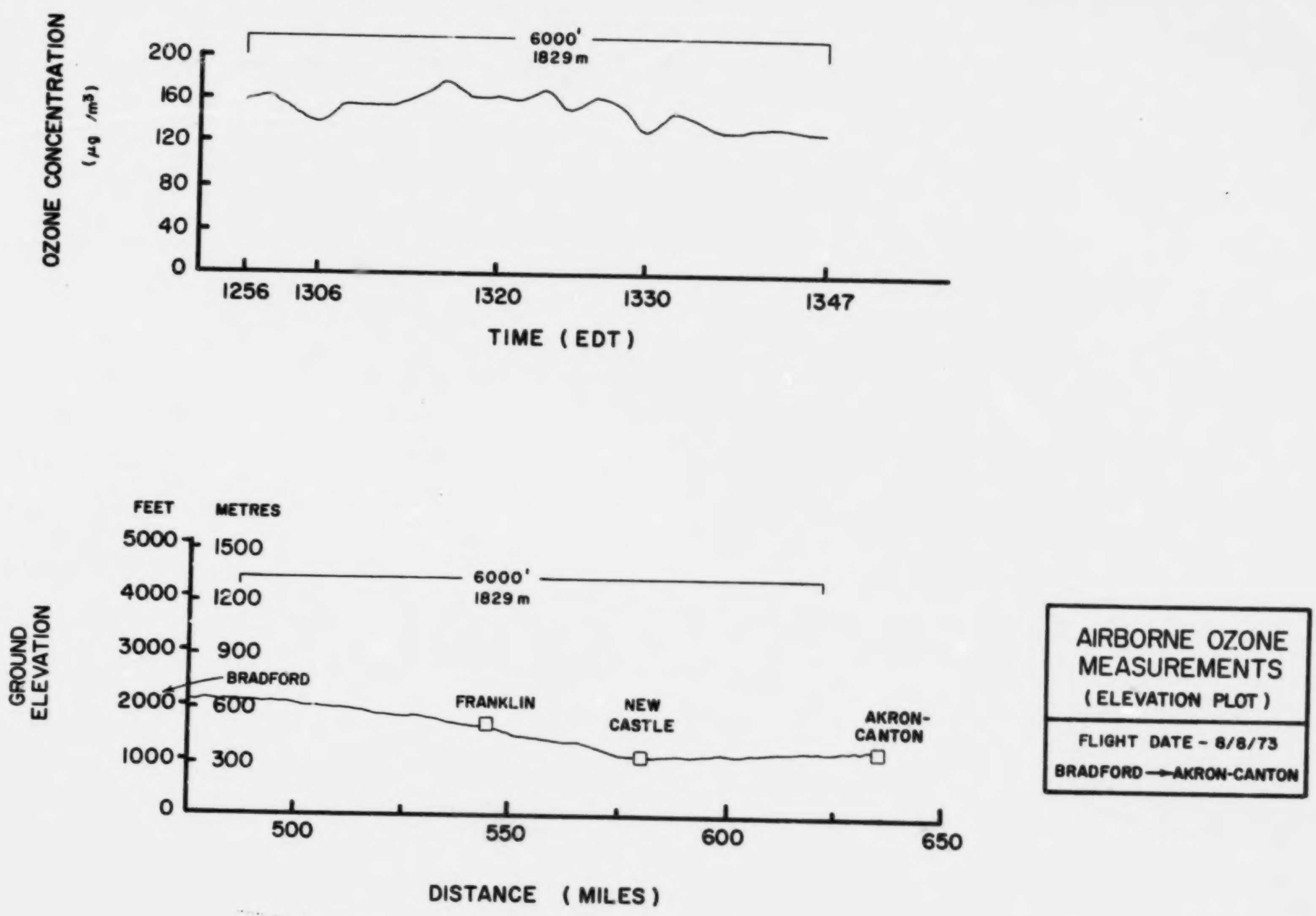


Figure 9. September 9, 1973, data acquisition flight.

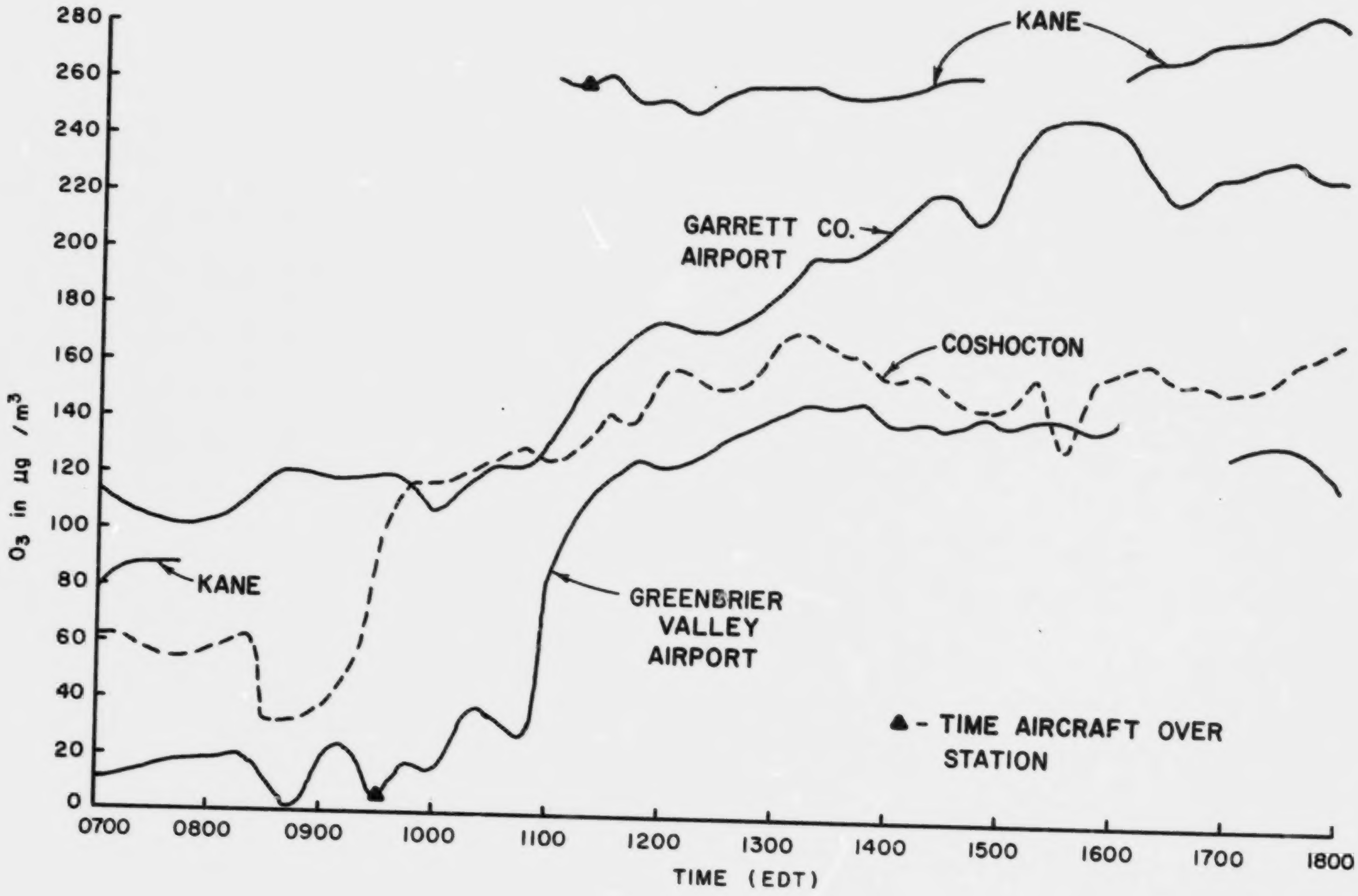


Figure 10. Ozone concentrations for Ausust 8, 1973, respective ground stations.

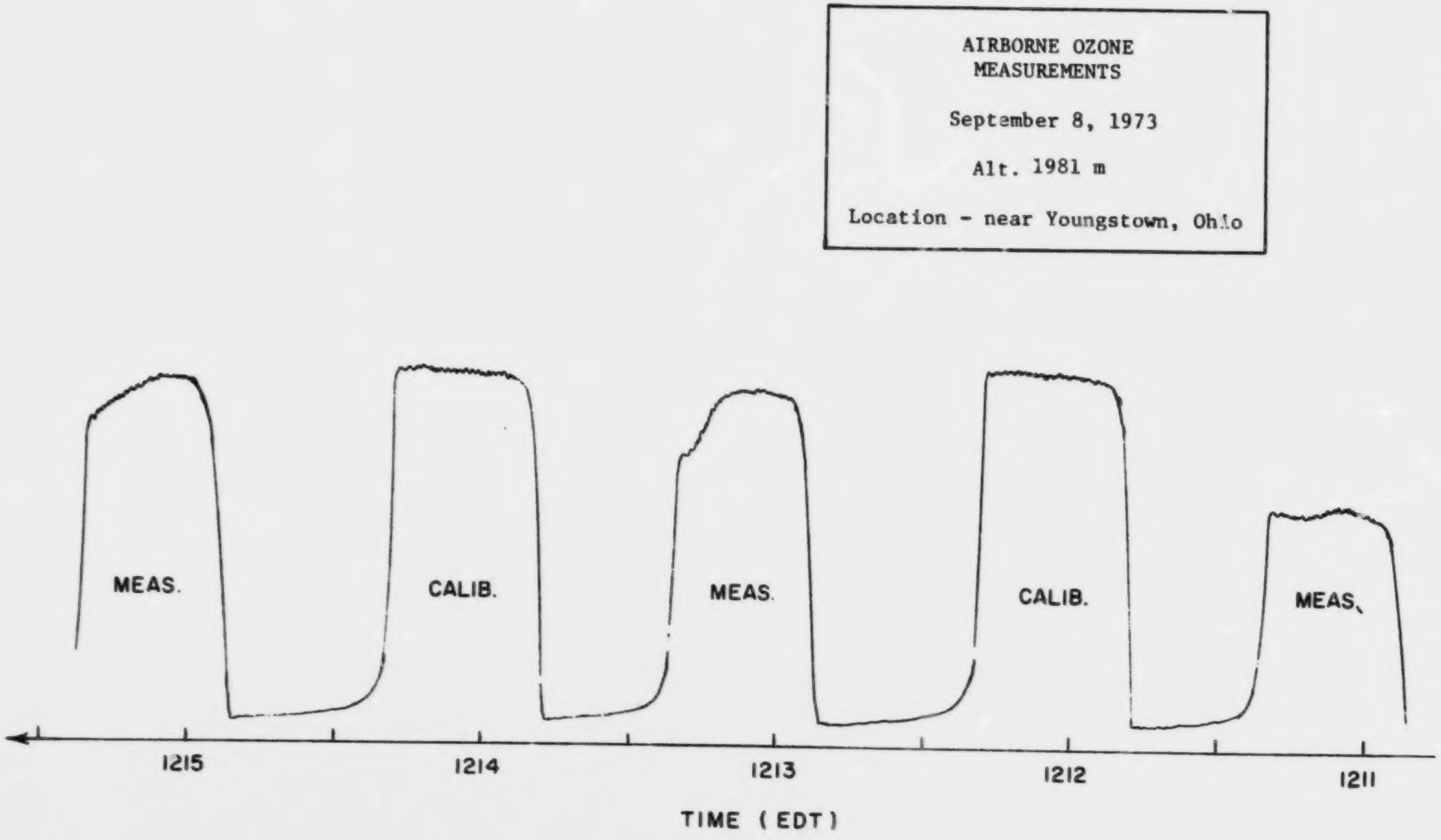


Figure 11. Illustratio of rapidly increasing ozone concentration.

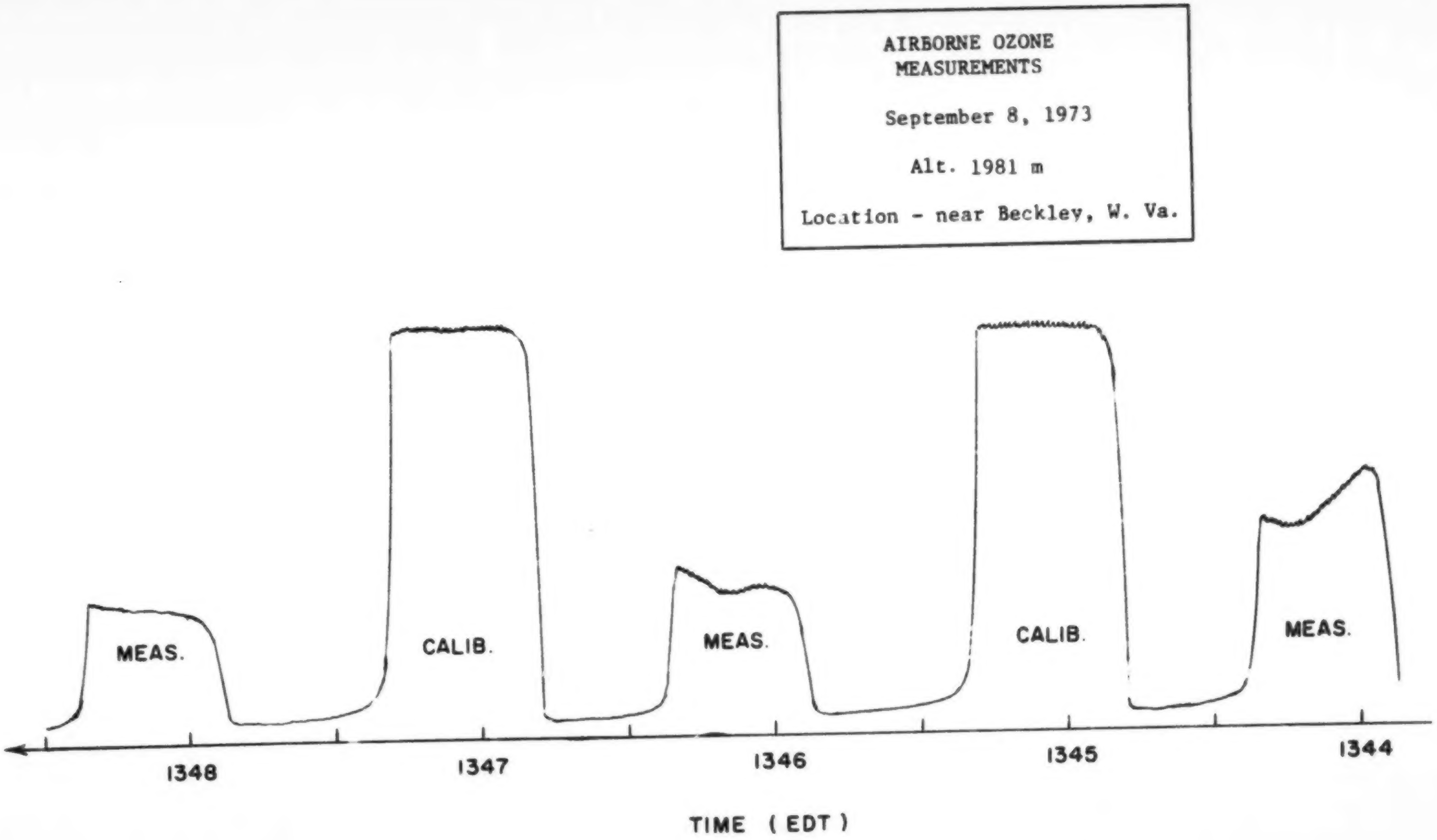


Figure 12. Illustration of rapidly varying ozone concentration

4.2 Data Acquisition Flight for September 11, 1973

The flight log was as follows:

a) Roundtrip flight to Greenbrier Valley Airport with a descent over the station, afternoon flight.

b) The flight was made under VFR conditions, a landing was made at the Greenbrier Valley Airport.

c) Flow rate tests were conducted in flight, which is the reason for the different altitudes flown for different legs of the flight path and the breaks in the data.

Data for this flight are given in Figures 13, 14 and 15. Vertical measurement data is presented in Figure 16 and fixed site measurements are given in Figure 17.

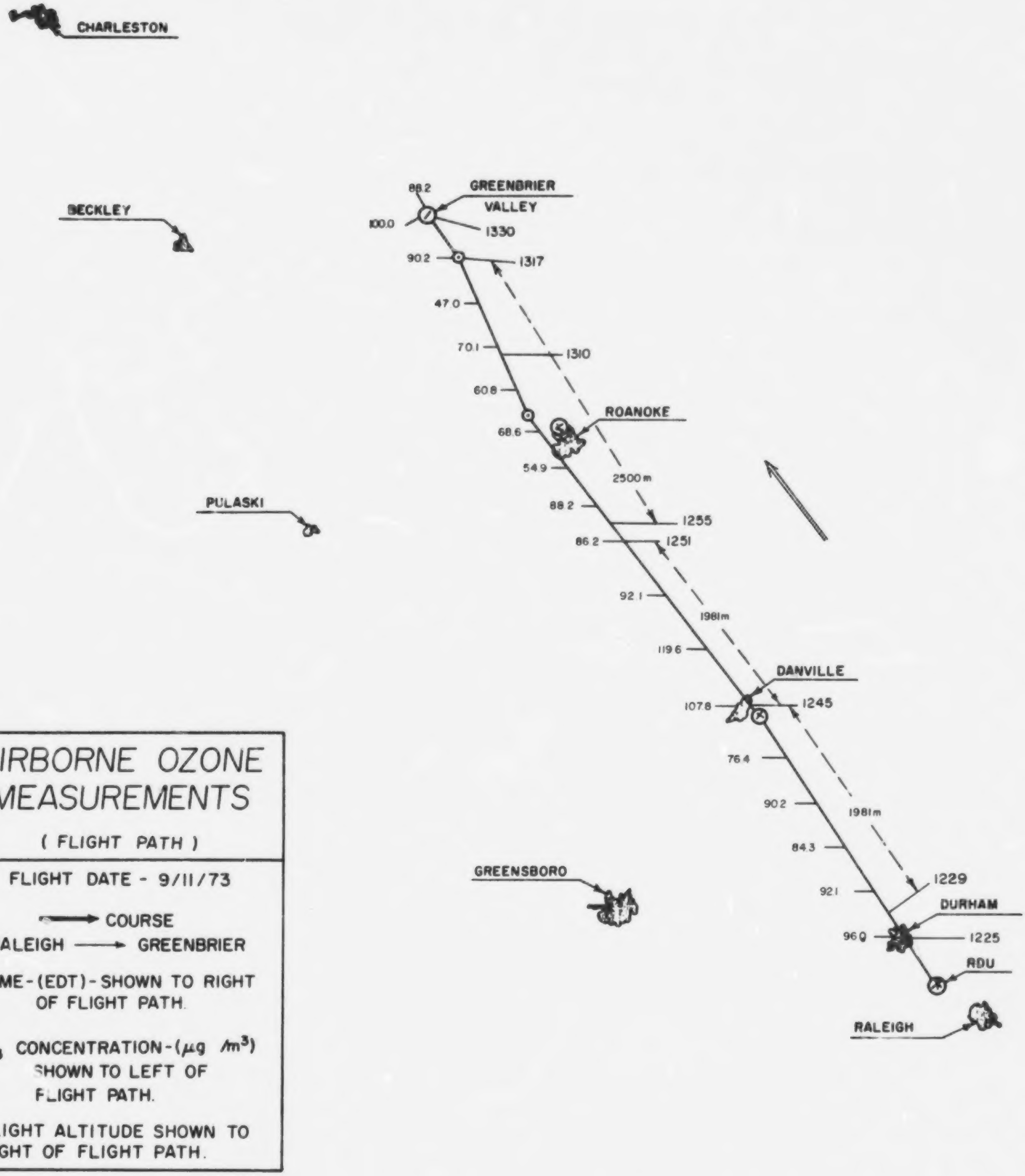

CHARLESTON
88.2
GREENBRIER
VALLEY
100.0
1330
BECKLEY
90.2
1317
47.0
70.1
1310
60.8
ROANOKE
68.6
54.9
2500m
PULASKI
88.2
1255
86.2
1251
92.1
1981m
119.6
DANVILLE
107.8
1245
76.4
90.2
1981m
84.3
GREENSBORO
1229
92.1
DURHAM
96.0
1225
RDU
RALEIGH
AIRBORNE OZONE MEASUREMENTS
(FLIGHT PATH)
FLIGHT DATE - 9/11/73
COURSE
RALEIGH ⟶ GREENBRIER
TIME-(EDT)-SHOWN TO RIGHT OF FLIGHT PATH.
O3 CONCENTRATION-(µg/m3) SHOWN TO LEFT OF FLIGHT PATH.
FLIGHT ALTITUDE SHOWN TO RIGHT OF FLIGHT PATH.

Figure 13. September 11, 1973, data acquisition flight.

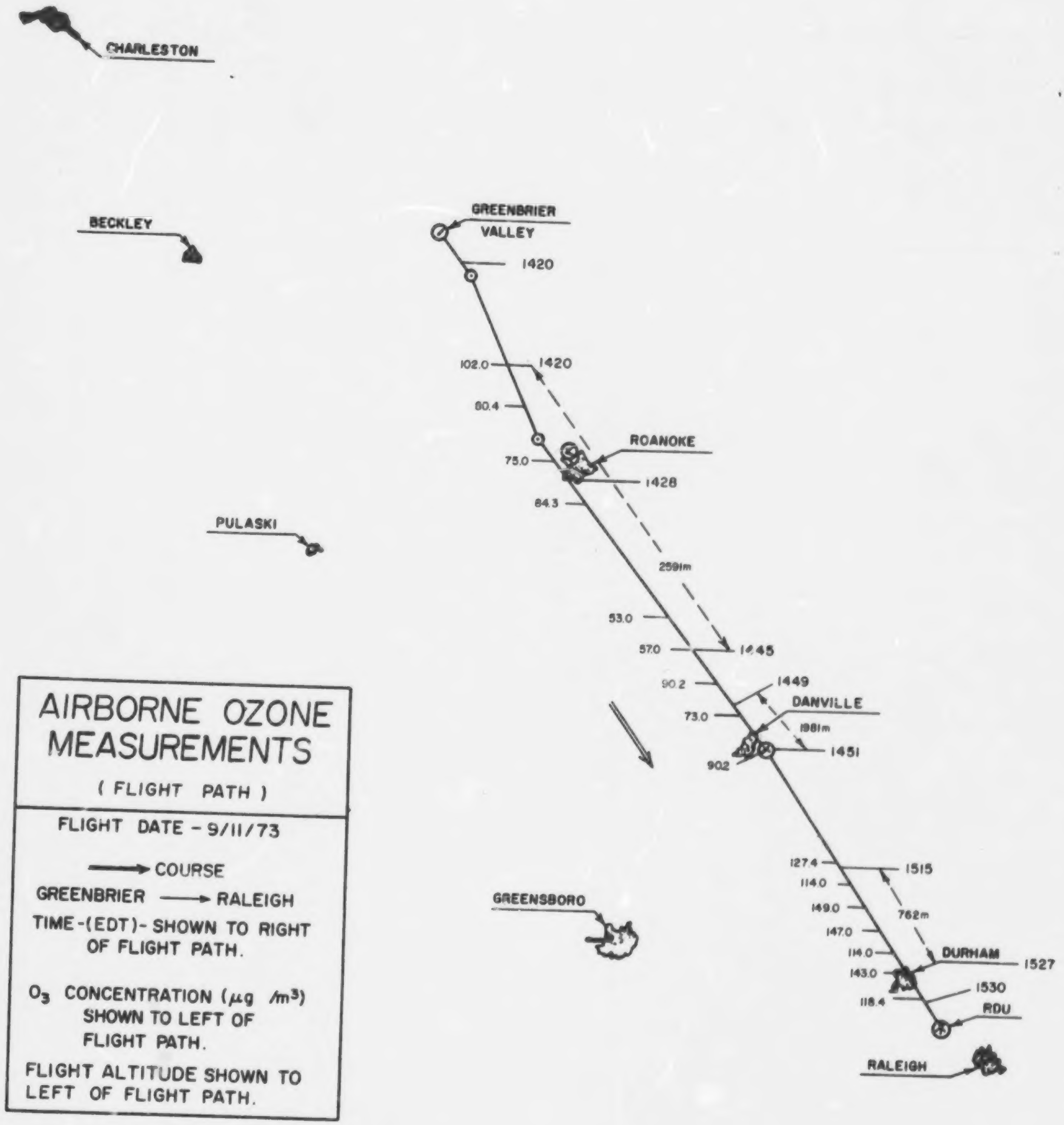

CHARLESTON
BECKLEY
GREENBRIER
VALLEY
1420
102.0
1420
80.4
ROANOKE
75.0
1428
84.3
PULASKI
2591m
53.0
57.0
1445
90.2
1449
DANVILLE
73.0
1981m
1451
90.2
127.4
1515
114.0
149.0
762m
147.0
GREENSBORO
114.0
DURHAM
1527
143.0
1530
118.4
RDU
RALEIGH
AIRBORNE OZONE
MEASUREMENTS
(FLIGHT PATH)
FLIGHT DATE - 9/11/73
COURSE
GREENBRIER → RALEIGH
TIME-(EDT)- SHOWN TO RIGHT OF FLIGHT PATH.
O3 CONCENTRATION (μg /m3) SHOWN TO LEFT OF FLIGHT PATH.
FLIGHT ALTITUDE SHOWN TO LEFT OF FLIGHT PATH.

Figure 14. September 11, 1973, data acquisition flight.

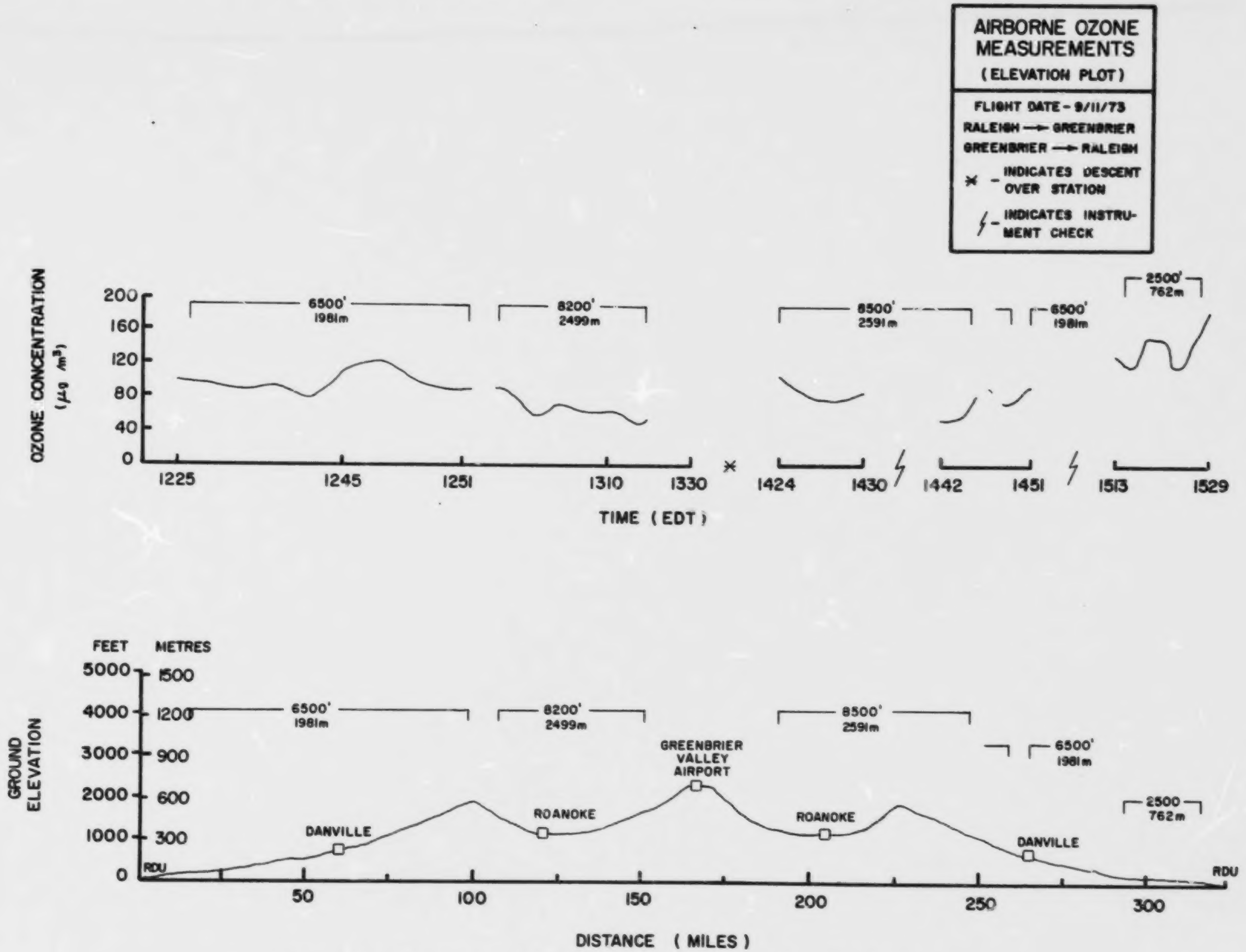


Figure 15. September 11, 1973, data acquisition flight.

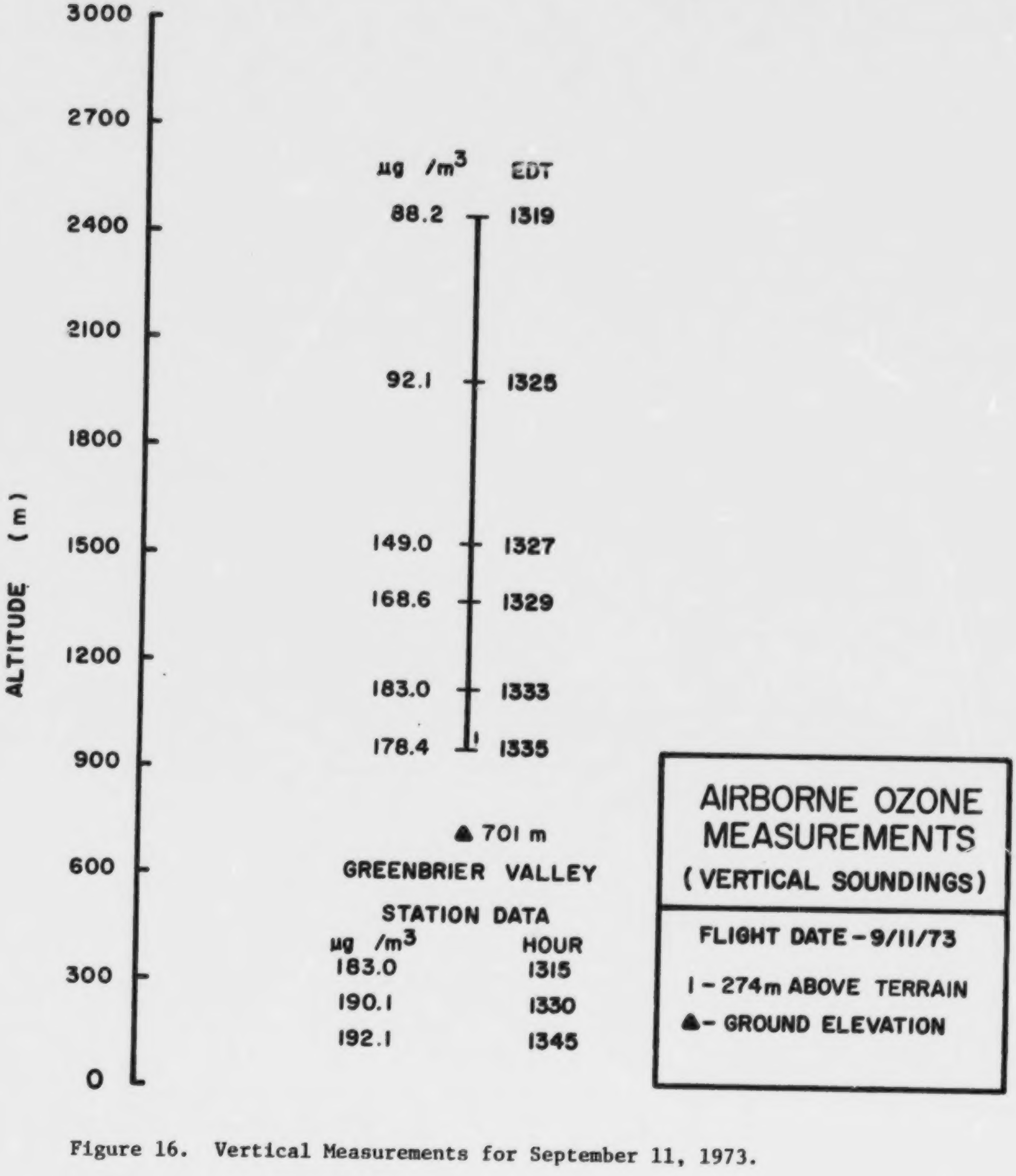


Figure 16. Vertical Measurements for September 11, 1973.

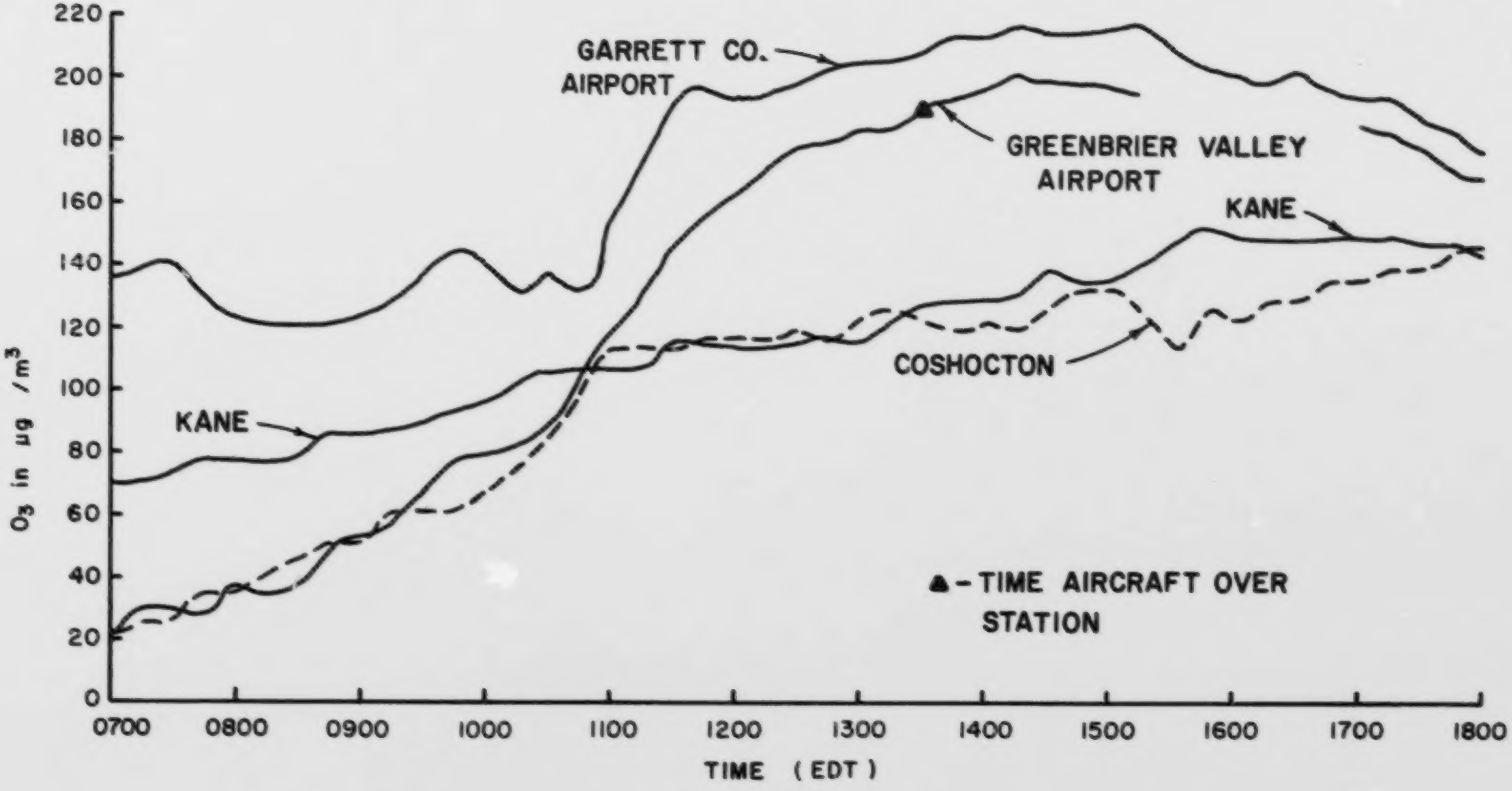


Figure 17. Ozone concentrations for September 11, 1973, respective ground stations.

4.3 Data Acquisition Flight for September 12, 1973

The flight log was as follows:

a) Flight originated at RDU and was flown under VFR conditions.

b) All legs of flight path from RDU to BFD were flown at 8500 feet; and from BFD to RDU an altitude of 9000 feet was maintained.

c) Descents in 2000 ft increments were made over each of the sampling sites.

d) Meteorological observations are tabulated for this flight.

Data are presented in Figures 18, 19 and 20 showing ozone concentration versus position or location. Vertical measurements over each of the fixed sites is given in Figure 21 along with ground station data for the three 15-minute periods which bracket the time of closest approach to the station. In-flight observations for the flight are given in Table 1. The fixed site data for the day of the data flight is given in Figure 22. An example of the strip chart recording for a rapidly changing concentration condition is shown in Figure 23.

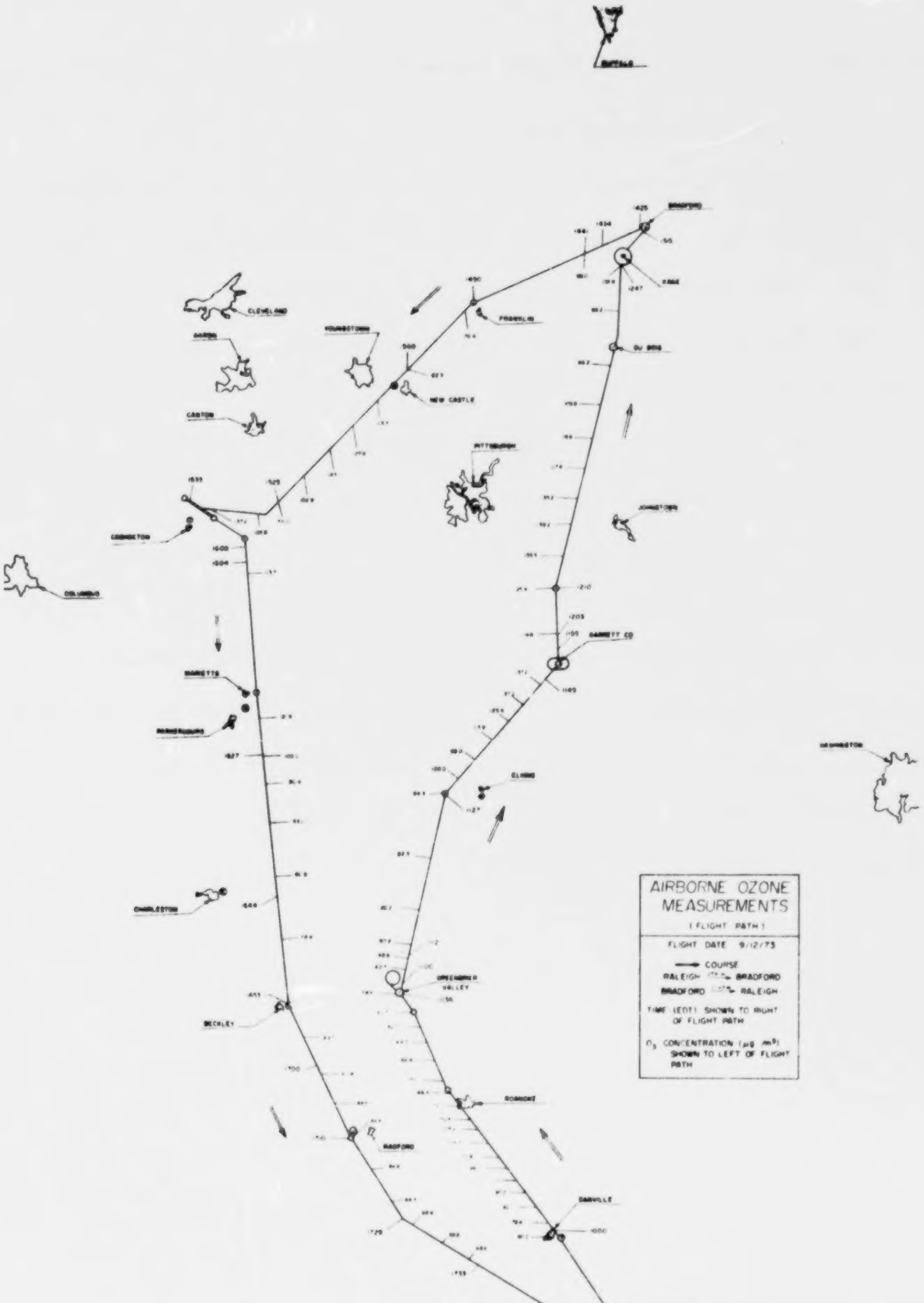

BUFFALO
BRADFORD
CLEVELAND
AKRON
YOUNGSTOWN
FRANKLIN
NEW CASTLE
CANTON
PITTSBURGH
DU BOIS
JOHNSTOWN
COSHOCTON
COLUMBUS
GARRETT CO
MARIETTA
PARKERSBURG
ELKINS
WASHINGTON
CHARLESTON
GREENBRIER VALLEY
BECKLEY
ROANOKE
RADFORD
DANVILLE
GREENSBORO
DURHAM
RDU
AIRBORNE OZONE MEASUREMENTS
(FLIGHT PATH)
FLIGHT DATE 9/12/73
COURSE
RALEIGH → BRADFORD
BRADFORD → RALEIGH
TIME (EDT) SHOWN TO RIGHT OF FLIGHT PATH
O3 CONCENTRATION (μg/m3) SHOWN TO LEFT OF FLIGHT PATH

Figure 18. September 12, 1973, data acquisition flight.

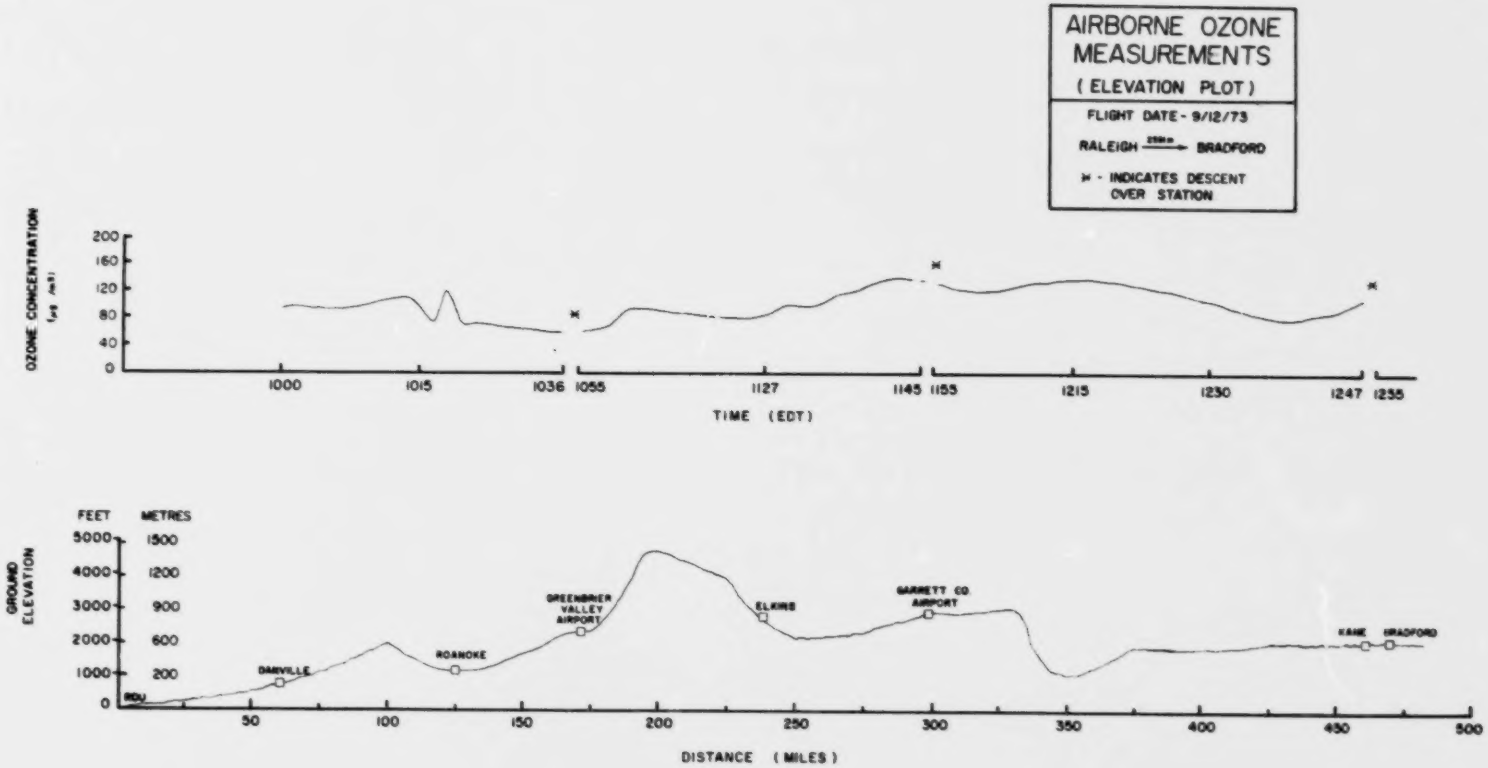


Figure 19. September 12, 1973, data acquisition flight.

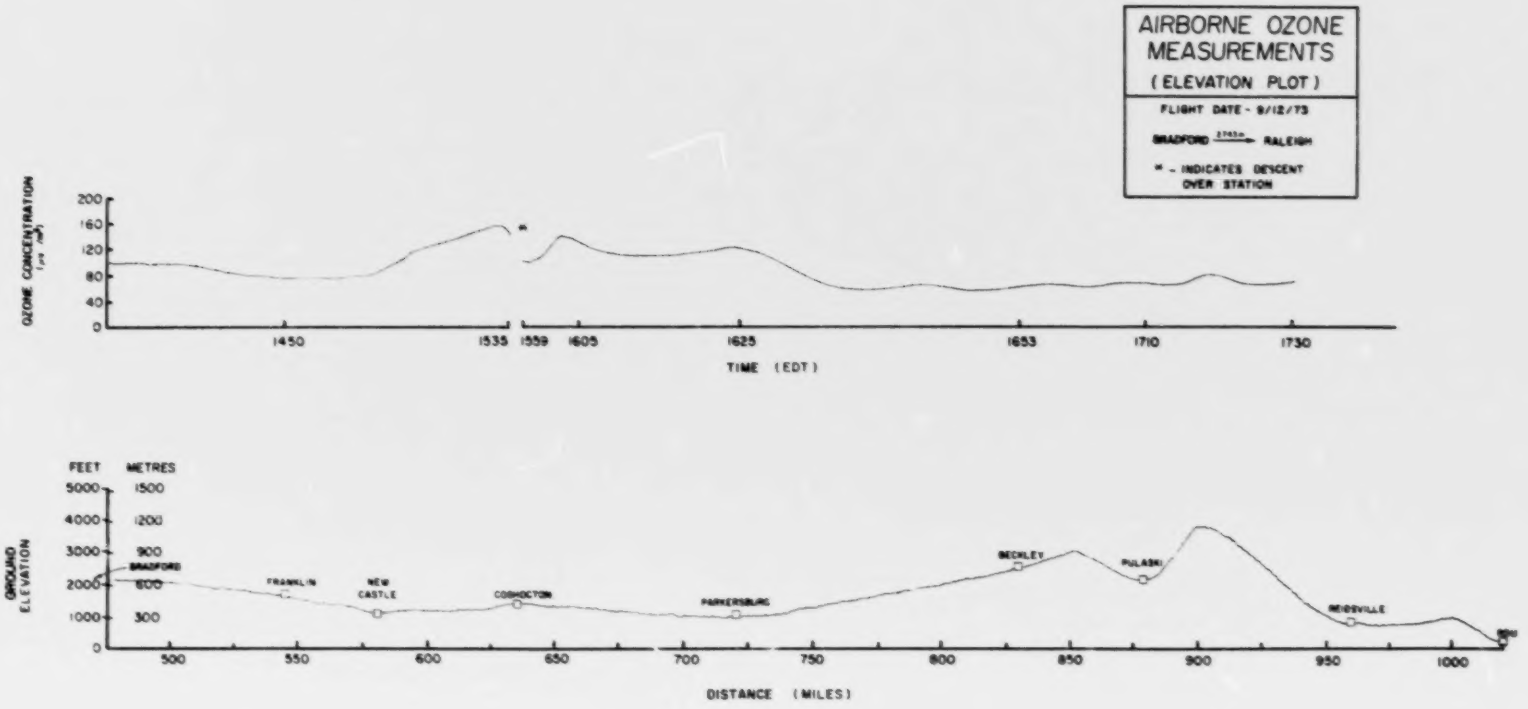


Figure 20. September 12, 1973, data acquisition flight.

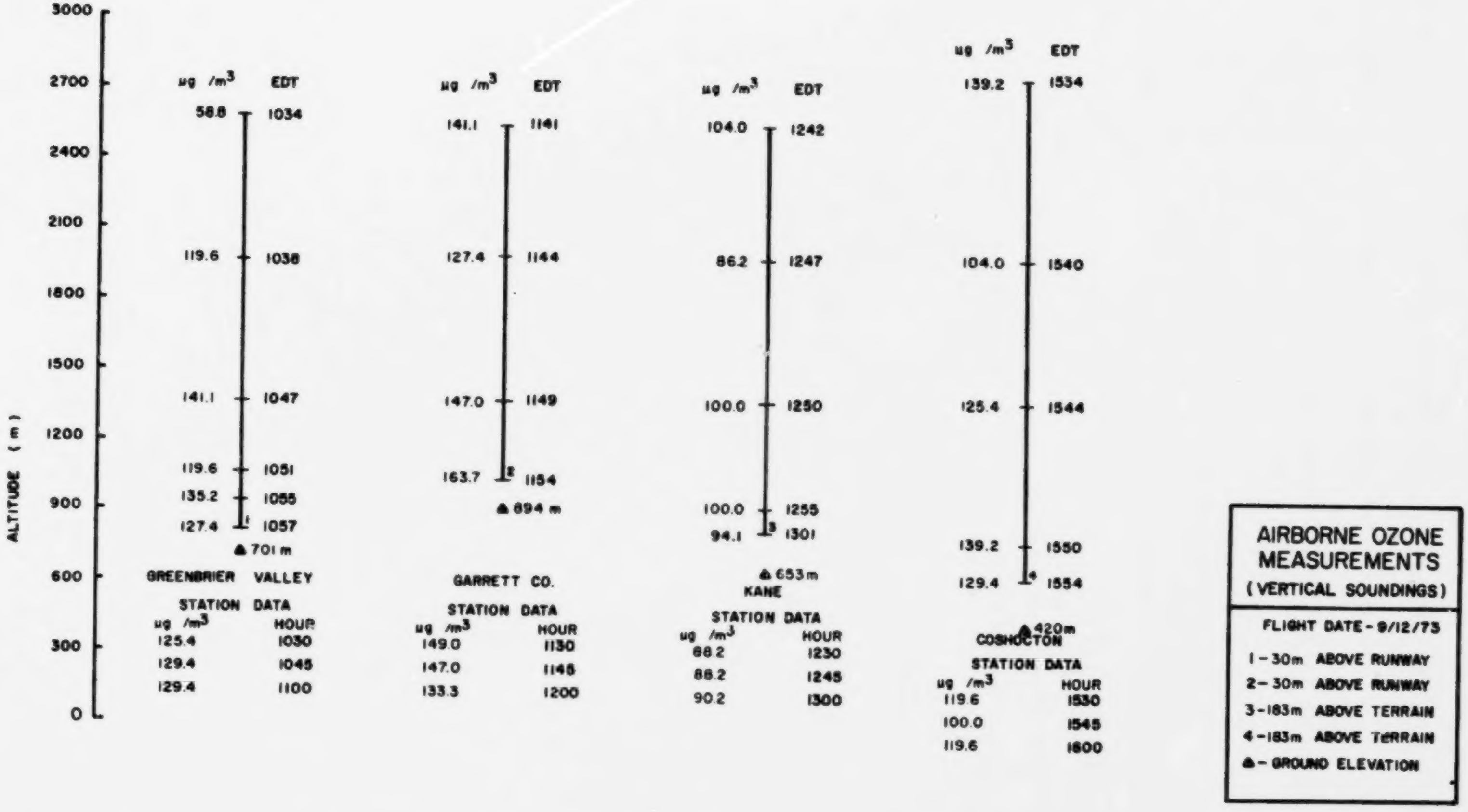


Figure 21. Vertical measurement for September 12, 1973, data acquisition flight.

INFLIGHT OBSERVATIONS - 9/12/73

The in-flight observations in Table 1 were made for the flight on 9/12/73. The location of the observations may be determined by locating the time on the ground track on the appropriate figure. The outside temperature was measured using the aircraft outside air temperature sensor. In general, climb and descents were made at a rate of 500 ft/min, the response time of the air temperature sensor was not known; the readings were made in approximately 500 ft increments, where practical.

Table 1
Flight Observation for September 12, 1973

Time (EDT)	Altitude (ft)	Outside Air Temp (°C)	Aircraft Attitude (C-climb) (L-level) (D-descending)	Observation
0946	6000	12	C	
	7500	9	C	Top of Haze
0950	8500	11.5	L	
0955	8500	10	L	Thin cloud layer around 700 ft
0959	"	8.5	L	
1007	"	9	L	
1013	"	10	L	
1018	"	12	L	
1037	8500	16	D	Over Greenbrier Valley
1045	6500	15	L	
1047	5500	-	D	Top of Haze level
1050	4500	14	L	
1112	8500	12	L	Thin scattered 6000 ft
1128	"	10		
1146	6500	8	D	
1153	4500	15	L	Cloud base 5500 ft
1203	8500	8	L	
1210	"	8	L	
1250	6500	3	L	Over Kane, Pa. site
1253	4500	9	L	"
1300	2500	14	L	"
1427	5000	6	C	
1432	7500	0	C	Cloud base 6500 ft
1434	8500	6	L	

Table 1 (Continued)

Meteorological Observations - 9/12/74

	Altitude ft)	Outside Air Temp (°C)	Aircraft Attitude (C-climb) (L-level) (D-descending)	Observation
1450	9000	5	L	
1502	"	6	L	
1514	"	7	L	
1516	"	8	L	
1525	"	9	L	
1537	6500	7	L	Over Coshocton, Ohio site
1542	4500	12	L	
1548	2500	17	L	
1552	2000	19	L	
1603	5000	9	C	
1604	6000	8	C	
	6500	7	C	Haze level
	7000	6.5	C	
	7500	8	C	
	8000	8	C	
	8500	8	C	Cloud Tops
1610	9000	10	L	
1644	9000	10	L	
1653	"	10	L	
1710	"	10	L	
1720	"	11	L	
1733	9000	12	D	
	8000	13	D	
	7500	14	D	
	7000	15	D	
	6500	15	D	Haze level
	6000	14	D	
	5500	15	D	
1742	5000	17	D	
1750	1500	26	L	Near RDU

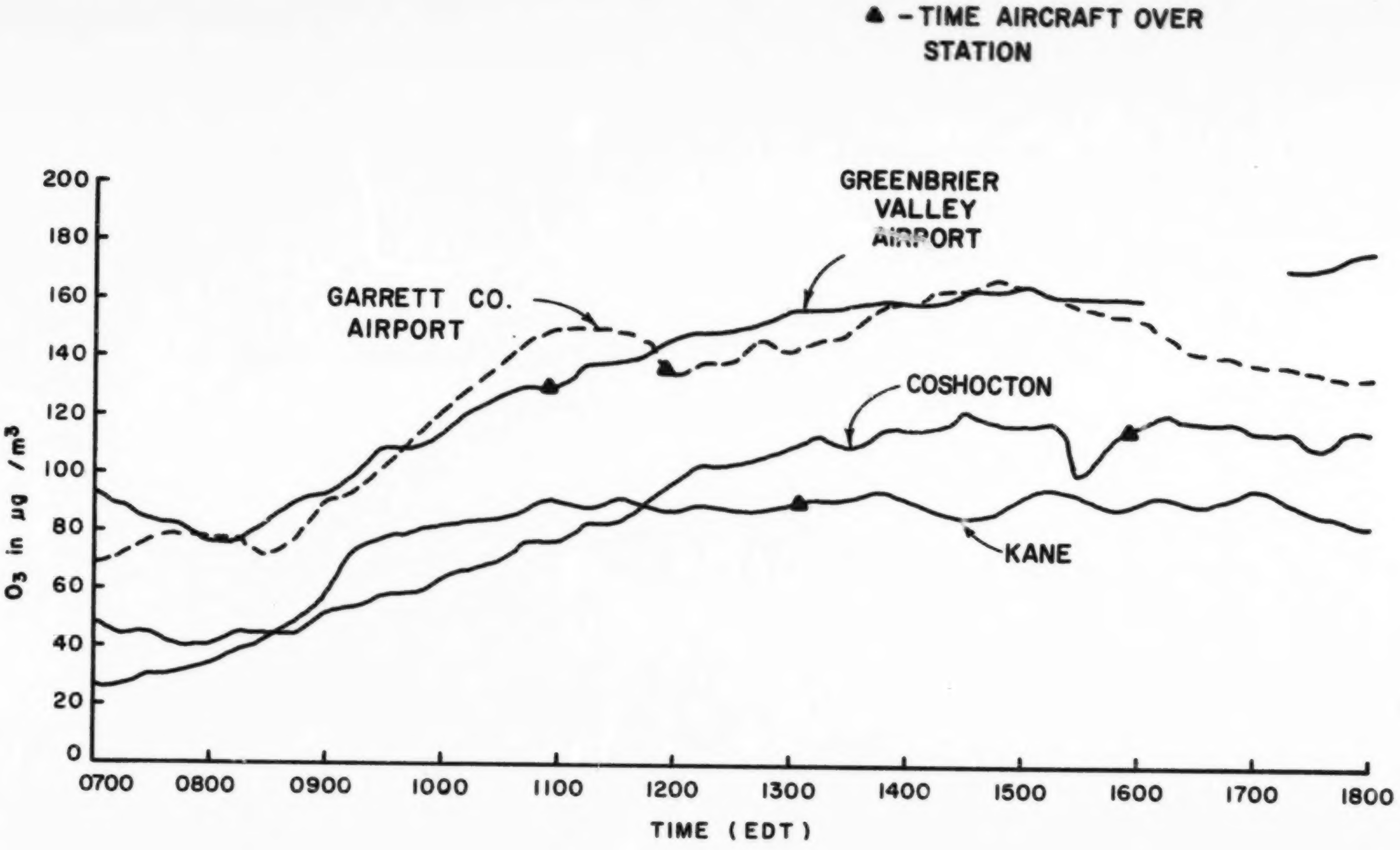


Figure 22. Ozone concentrations for September 12, 1973, respective ground stations.

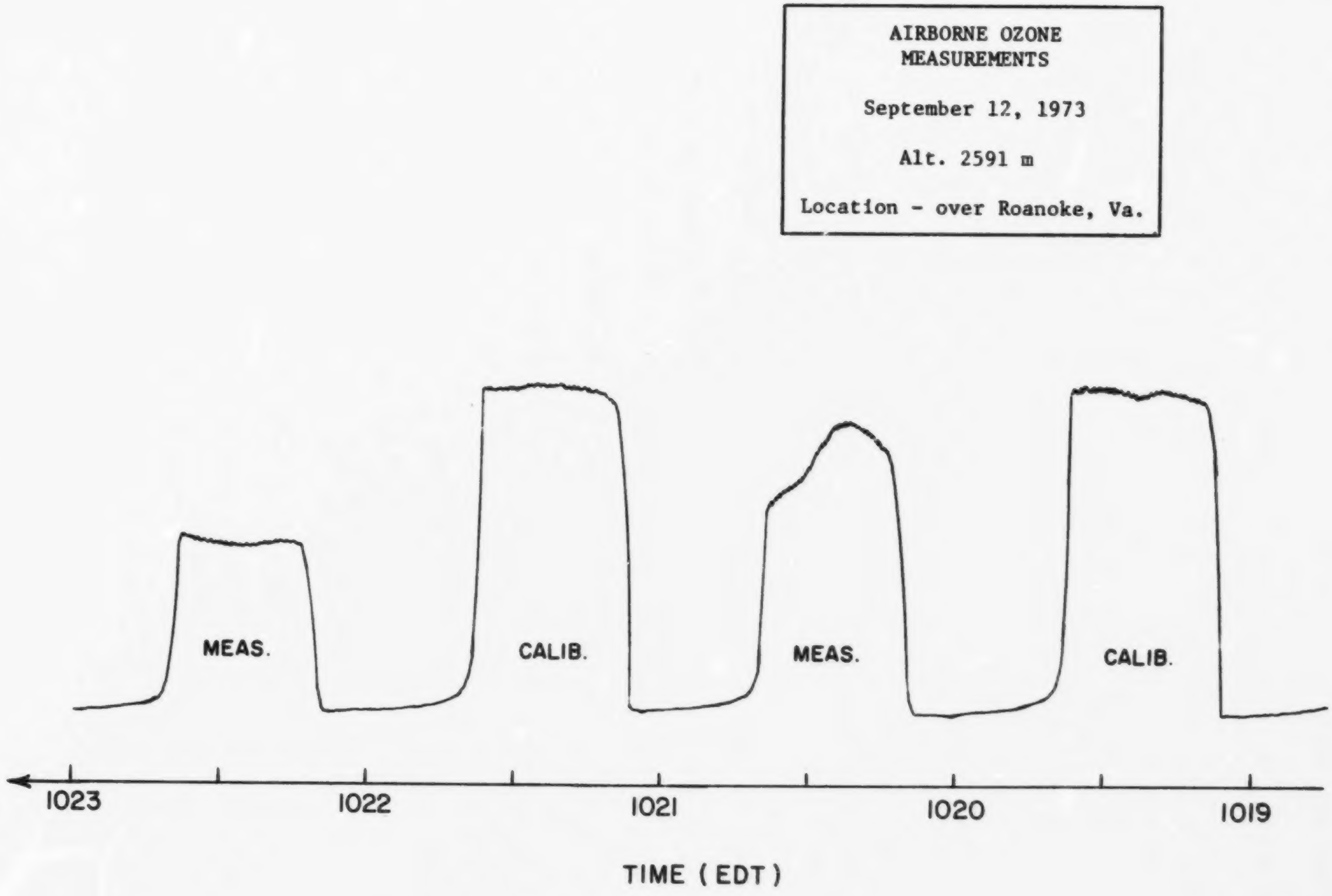


Figure 23. Illustration of rapidly changing ozone concentration.

5.0 SUMMARY AND CONCLUSIONS

The purpose of the program was to obtain some measurements of the ozone concentration in the troposphere in the region bounded by the fixed monitoring sites operated under Contract 68-02-1077.

A solid phase chemiluminescent ozone meter with internal calibration unit was installed and flown in a C-45 aircraft. Calibrations were performed on the ground and the flow rate was monitored in-flight. In addition, tests were conducted in-flight and on the ground to obtain and verify the altitude correction factor. The equipment functioned well in the aircraft; vibration was not a problem; the power sources were adequate and stable.

Flights were made both under VFR and IFR conditions. During IFR conditions, it was not feasible to make descents over the sampling sites and the altitude requested was contingent on approval of the flight plan. Operationally, it was more practical to make descents to the selected altitudes, (i.e., acquire the desired data at one altitude and then descend to the next altitude) over the station than it was to climb sequentially to successive altitudes.

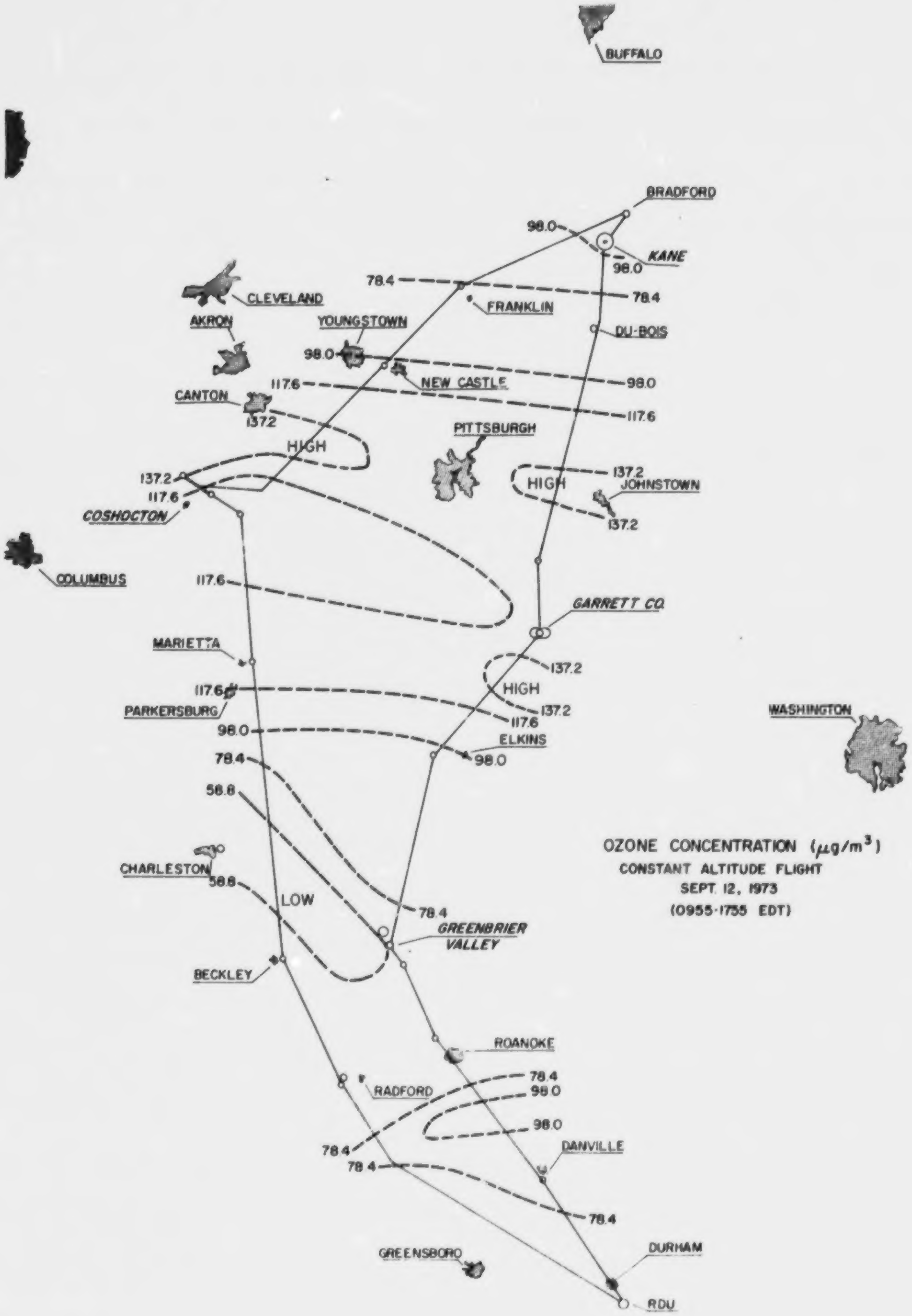
Inspection of the data on the strip chart records indicated that the ozone concentration was stable over the period of the sample, which represented 30 sec in time and approximately 1.44 miles spatially at the normal cruising speed. Rapid changes in ozone concentrations were observed in some regions. Verification of the aircraft data by flying as close to the fixed monitoring sites as feasible proved to be practical in most instances. The dynamic checks made in this manner showed good correlation between the ground station and the airborne ozone measurements, thus confirming the satisfactory operation of the airborne units (See Table 2).

Table 2. COMPARISONS GROUND AND AIRCRAFT OZONE DATA

	Groundreading (15 min. avg.)	Time	Aircraft	Time	Height Above Ground
Greenbrier Valley	129.4 $\mu g/m^3$	1100	127.4 $\mu g/m^3$	1057	100 ft
Garrett Co.	145.0 $\mu g/m^3$	1145	160.7 $\mu g/m^3$	1154	100 ft
Kane, Pa.	90.2 $\mu g/m^3$	1300	94.1 $\mu g/m^3$	1301	600 ft
Coshocton, Ohio	119.6 $\mu g/m^3$	1600	129.4 $\mu g/m^3$	1554	600 ft

The isopleths drawn in Figure 24, which shows O_3 concentrations during the flight of 12 September 1973, are speculative, but tend to show that the O_3 behavior is regional and not local in nature. The horizontal gradients are small and much interpolation between data points has been used.

There is a temptation to ascribe various features of lower and higher O_3 values to nearby urban areas, but the data are too few. Also, interpretation would require a more detailed past history of the air as well as a knowledge of the chemical input from the various cities. Both increases and decreases in O_3 values appear downwind of urban areas. There is a corridor of low values of about 59 $\mu g/m^3$ downwind of Charleston, West Virginia and an area of higher values (137 to nearly 157 $\mu g/m^3$) downwind of the cluster of cities, Cleveland, Akron, and Canton.


BUFFALO
BRADFORD
98.0
KANE
98.0
78.4
78.4
CLEVELAND
FRANKLIN
AKRON
YOUNGSTOWN
DU-BOIS
98.0
NEW CASTLE
98.0
117.6
117.6
CANTON
137.2
PITTSBURGH
HIGH
137.2
HIGH
137.2
JOHNSTOWN
117.6
137.2
COSHOCTON
COLUMBUS
117.6
GARRETT CO.
MARIETTA
137.2
117.6
HIGH
PARKERSBURG
137.2
117.6
WASHINGTON
98.0
ELKINS
98.0
78.4
58.8
CHARLESTON
58.8
LOW
78.4
GREENBRIER VALLEY
BECKLEY
ROANOKE
78.4
98.0
RADFORD
98.0
78.4
DANVILLE
78.4
78.4
GREENSBORO
DURHAM
RDU

OZONE CONCENTRATION ($\mu g/m^3$)
CONSTANT ALTITUDE FLIGHT
SEPT. 12, 1973
(0955-1755 EDT)

Figure 24. Ozone concentration, constant altitude flight, September 12, 1973. (Observed concentration values have been reduced to standard conditions)

Extrapolation of temperature sonde data from pertinent weather stations on September 12 (confirmed by temperature measurements taken from the aircraft) indicated the presence of an inversion located somewhere between 5000 and 8500 feet aloft over the four sampling sites.

The vertical distribution of ozone data indicates that the relationships between ground values and data aloft are not obvious. The O_3 vertical profiles shown over the Greenbrier Valley Airport (Lewisburg) present a picture of a low value of O_3 above the inversion and O_3 generated from ground-sourced precursors below the inversion level. Ozone measured at and near the ground at the Greenbrier Valley Airport was generated in the lower atmosphere and was not transported from the stratosphere by vertical turbulence.

Another implication of the vertical data is that the O_3 or O_3 precursors had moved into the ground sampling area at a level below the altitude of the aircraft, but that at times surface influence on O_3 concentration can extend several thousand feet.

Measurements made from an aircraft have proved extremely interesting and informative. The flights made as part of this project suggest that a greater sampling frequency would yield more than a one for one increase in useful information.

6.0 REFERENCES

1. "Ozone Chemiluminescent Study," Final Report, Under NAPCA Contract No. CPA-22-69-7, by Research Triangle Institute, December 1969.

2. "Field Evaluation of New Air Monitoring Systems," Final Report under EPA Contract No. CPA-70-101, by Research Triangle Institute, May 1972.

3. Hodgeson, J. A., et al., "Laboratory Evaluation of Alternate Chemiluminescent Approaches for the Detection of Atmospheric Ozone," presented September 1970 ACS Meeting.

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